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PHYSICAL REVIEW

ATMOSPHERIC IONIZATION BY COSMIC RADIATION*

By E. O. Hulburt

Naval Research Laboratory

(Received November 22, 1930)

Abstract

From Millikan's measurements of the intensity and the absorption coefficients of cosmic radiation the ionization in the atmosphere is calculated from sea level to 60 km. The electron density is negligibly small in this region. The ion density increases with the height to 3.5×10^3 ion pairs cm^{-3} at about 50 km and is roughly constant above this to 60 or 70 km where the solar ultraviolet light ionization sets in. The 50 km ion bank refracts appreciably radio waves longer than 12 km and being unchanged with the day and night accounts for the propagation of waves longer than 12 km, which are known to show no marked diurnal variations. The agreement with the facts of long radio waves indicates that there exists in the high atmosphere but little cosmic radiation of less penetration than Millikan has already detected.

By considering the effect of the earth's magnetic field on high speed electrons the "run away" electron hypothesis of C. T. R. Wilson to account for cosmic radiation is shown to lead to a distribution most intense at low latitudes and feeble at high latitudes, thereby being in disagreement with Millikan's observation of the constancy of the cosmic radiation with latitude.

1. It is pretty generally accepted, as a result of the work of Hess, Bauer, Swann, Mauchly, Millikan and others,[1] that the ionization in the lower atmosphere is caused primarily by a penetrating radiation of cosmic origin. Over the land in the levels of the atmosphere below about 2 km the radiation from radio-active materials in the earth may cause an appreciable part, as much as a half or more, of the ionization. But from levels above 2 km over the land, and from about sea level upward over the sea, up to the limit of direct observation[2] at about 15 km, the measurements support the view that the ionization is caused by a cosmic radiation coming in from all directions and absorbed exponentially in its passage through the atmosphere.[2,3] In the present paper the ionization due to cosmic radiation is calculated from sea level to about 70 km, where the Kennelly-Heaviside layer begins, and is

* Published with the permission of the Navy Department.

[1] See Hess "The Electrical Conductivity of the Atmosphere and its Causes" (1928), and references cited throughout the present paper.

[2] Millikan and Cameron, Phys. Rev. **31,** 163 (1928).

[3] Millikan and Bowen, Phys. Rev. **22,** 198 (1923); **27,** 353 (1926); Millikan and Otis, Phys. Rev. **27,** 353 and 645 (1926): Millikan and Cameron, Phys. Rev. **28,** 851 (1926); etc.

found to agree with certain facts of the propagation of long wireless waves. A calculation of the ionization by cosmic radiation was made by Benndorf.[4] The more recent observations of cosmic radiation were of course not available to him and he did not consider such actions as the attachment of electrons to oxygen molecules, etc.; the present calculation which includes these factors is thought to be more nearly correct. In section 6 it is shown that the "run away" electron hypothesis of C. T. R. Wilson is inadequate to account for the observed facts of cosmic radiation.

2. The Rate of Productions of Ions in the Atmosphere by Cosmic Radiation

The second column of Table I gives the values of n, the total number of molecules and atoms cm^{-3}, assuming no hydrogen in the atmosphere, for various heights z above sea level. The values of n are from Maris' tables[5] for winter day conditions in temperate latitudes. From $z=0$ to 100 km n is given, within an approximation sufficiently good for the present calculations, by

$$n = n_0 \epsilon^{-pz}, \tag{1}$$

where n_0 is the value of n at sea level and $p=1.38\times10^{-6}$ for z in cm. Since the curve of log n against z is not exactly a straight line p varies a little with z; for z from 100 to 300 km the average value of p is 1.21×10^{-6}, a value used in a former paper.[6] For summer night conditions n is much the same as the values of Table I, for summer day and winter night conditions n is slightly different. We are content, however, to use the winter day values to represent a rough average condition of the atmosphere.

Table I.

1 z	2 n	3 q'	4 q	5 I	6 Temp.	7 α	8 y
0 km	2.68×10^{19}	1.4	1.4	1.09×10^{-6}	300°K	0.766×10^{-25}	8.25×10^{2}
10	6.77×10^{18}	21.1	5.32	1.51×10^{-4}	260	3.3 "	1.55×10^{3}
20	1.85×10^{18}	54.1	3.72	3.86 "	220	5.4 "	1.92 "
30	4.00×10^{17}		1.08	5.17 "	220	5.4 "	2.22 "
40	8.59×10^{16}		0.24	5.30 "	260	3.3 "	2.91 "
50	2.26×10^{16}		6.26×10^{-2}	5.31 "	300	2.3 "	3.48 "
60	5.58×10^{15}		1.54×10^{-2}	5.31 "	300	2.3 "	3.48 "
70	1.48×10^{15}		4.21×10^{-3}	5.31 "	300	2.3 "	3.48 "
80	3.71×10^{14}		1.02×10^{-3}	5.31 "	300	2.3 "	3.48 "

Millikan, Bowen, Otis and Cameron[2,3], by sending up apparatus in balloons, made direct observations of the ionization due to cosmic radiation up to a height of about 15 km. They calculated[2] the absorption coefficient μ and the values of q' from sea level to 20 km and at the "top" of the at-

[4] Benndorf, Phys. Zeits. **27,** 686 (1926), see also Pederson, "The Propagation of Radio Waves," page 62 (1927).

[5] Maris, Terr. Mag. and Atmos. Elec. **33,** 233 (1928); **34,** 45 (1929).

[6] Hulburt, Phys. Rev. **31,** 1018 (1928).

mosphere, using the Gold[7] tables for the case of radiation entering the atmosphere equally distributed in all directions above the horizontal plane. They found that the radiation became softer, i.e., less penetrating, as z increased, the average absorption coefficient μ per meter of water from $z=0$ to 0.9 km being 0.23 and for z greater than 0.9 km being 0.25. q' is the number cm^{-3} sec^{-1} of ion pairs which would be produced by the cosmic radiation in 1 cm^3 of air at sea level pressure placed at various heights in the atmosphere. The values of q' given in column 3, Table I, are taken from their Table IV, ref. 2.

In dealing with the atmosphere it is more convenient to use q instead of q', where q is the number of ion pairs cm^{-3} sec^{-1} produced in the atmosphere by the cosmic radiation. Then

$$q = q'n/n_0. \tag{2}$$

The values of q calculated from q' for $z=0$ to 20 km are given in column 4, Table I. With $\mu=0.25$ per meter of water the molecular absorption coefficient β of atmospheric molecules, taken to be four parts nitrogen to one part oxygen, is 1.20×10^{-25}, on the assumption that β is proportional to the mass of the absorbing layer. β is defined in the usual way by

$$dI = -I\beta n dz, \tag{3}$$

where dI is the reduction in the intensity of radiation I erg cm^{-2} sec^{-1} in passing through a thickness dz cm of n atmospheric molecules cm^{-3}. Assuming that all of the absorbed energy goes into producing ions,

$$q = I\beta n/w, \tag{4}$$

where w is the work of ionization of the atmospheric particles. For oxygen and nitrogen atoms w is 2.15×10^{-11} and 2.32×10^{-11} erg, corresponding to ionization potentials 13.48 and 14.56 volts, respectively, and a little more for the molecules. With (4) I was calculated directly from the known values of q for $z=0$, 10 and 20 km and was continued into the higher levels by means of the Gold table.[7] The values of I are in column 5, Table I. From I and (4) q was calculated for the levels above 20 km, column 4, Table I. The extrapolation into the high levels assumed that β was constant throughout the region from $z=20$ to 60 km, i.e., that there exists no cosmic radiation of μ greater than 0.25. The evidence from wireless waves, section 5, indicates that this assumption is probably not much in error.

The total rate of production of electrons and positive ions by cosmic radiation in a 1 cm^2 column of the atmosphere from 60 km to interplanetary space is $\int_6^\infty q dz = 1.54\times10^{-2}/1.21\times10^{-6} = 1.28\times10^4$. This is much less than the production of ionization by the ultraviolet light of the sun, which amounts to 2×10^8 electrons and positive ions sec^{-1} in a 1 cm^2 vertical column above 180 km and many more below this level.[6,8] It is concluded that the

[7] Gold, Proc. Roy. Soc. **82,** 43 (1909).
[8] Hulburt, Phys. Rev. **34,** 1167 (1929).

ionization caused by cosmic radiation in levels above 60 km is inappreciable compared to that produced by solar ultraviolet light in all latitudes at all hours of the day and night.

3. The Ions and Electrons in the Atmosphere Caused by Cosmic Radiation

It is assumed that the cosmic radiation ionizes the air molecules and atoms to produce electrons and positive ions. The electron density y_e, assuming the loss of electrons arises only from recombination with positive ions and attachment to neutral oxygen molecules, is given by the steady state equation

$$q = \alpha_e n y_e^2 + bn' y_e, \tag{5}$$

where α_e is the J. J. Thomson[9] recombination coefficient for electrons and positive ions and b is the coefficient of attachment of electrons to oxygen molecules.[6] n' is the density of oxygen molecules. For $z=0$ $\alpha_e=0.52\times10^{-23}$, $b=8.3\times10^{-14}$ and putting $q=1.4$ into (5) gives $y_e=3\times10^{-6}$. y_e increases with z, but even at $z=60$ km y_e is only of order 10^{-3}. Therefore the electron density in these levels due to the ionizing action of cosmic rays is very small, being much less than 1 electron cm^{-3}. Further, the loss of electrons by attachment to oxygen molecules exceeds by several orders of magnitude the loss by recombination with positive ions. For example at $z=0$ $bn'y_e=1.4$ and $\alpha_e n y_e^2=1.3\times10^{-15}$, and at 60 km are equal to 1.5×10^{-2} and 10^{-13}, respectively. Therefore the electrons do not remain free very long but become attached to oxygen molecules almost as fast as they are formed. We may then take the values of q of column 4, Table I, to be the rates of production of ion pairs and calculate the ion densities which exist in a steady state.

For this case y, the number of ion pairs cm^{-3}, is given by

$$q = \alpha n y^2, \tag{6}$$

where α is the recombination coefficient of positive and negative ions.[9] α is a function of the temperature and the molecular density n for n greater than 10^{18}; the values of the winter day temperatures and of α are given in columns 6 and 7, Table I. The values of y calculated from (6) are given in column 8, Table I, and are plotted as abscissas against z as ordinate in Fig. 1. The values of y for winter night and for summer day and night are the same as those of Fig. 1 within 40%. The ion curve of Fig. 1 was obtained omitting diffusion. This is justifiable, for from Eq. (5), ref. 6, the rate of increase of ions due to diffusion is small compared to q for levels below 80 km. Winds would not be expected to disturb the curve very much. With the values of q of column (4), Table I, it takes roughly 10, 34 and 196 minutes to build up the steady state values of y at $z=0$, 30 and 40 km, respectively. Therefore the air must move upwards or downwards with velocities of the order of kilometers per minute in order to change the ion curve. Such movements seem improbable under ordinary circumstances.

[9] Thomson, Phil. Mag. **47**, 337 (1924); see also ref. 6 and 8 for a discussion of these coefficients.

4. Agreement with Observation

The value 825 ion pairs at sea level of Table I agrees with observation during fine weather, although, to be sure, we can not regard the present calculation, which omits such well-known effects in the lower atmosphere as water vapor, dust, ion clustering, ionization due to the splashing of waves, etc., as being a very complete statement of sea level conditions.

The ion layer of Fig. 1 will not cause appreciable absorption of wireless waves, even for those as long as 100 km. It will, however, refract long waves. The shortest wave, denoted by λ_s, ref. 6, which will be turned back to the earth is 11 km in length, and this only when incident on the layer at as near grazing incidence as possible, in which case the rays leave the earth tangentially (Eq. (26), ref. 6). Waves shorter than 11 km will pierce through the cosmic ion layer at 50 km to be refracted in the higher lying ionization

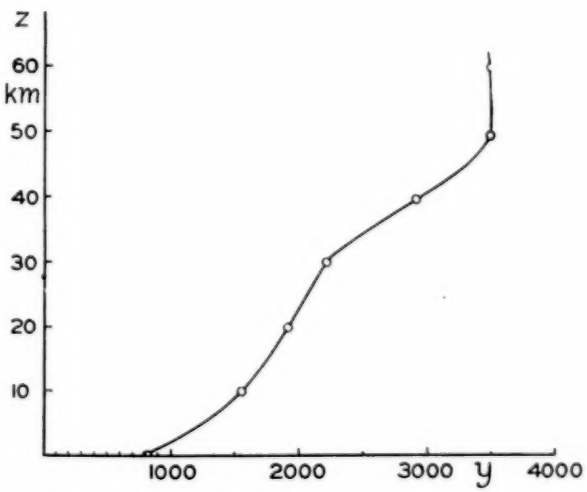

Fig. 1. Density y of ions pairs in the atmosphere caused by cosmic radiation.

above 70 km caused by the solar ultraviolet light. As the wave-length increases beyond 11 km the wave is refracted downward at decreasing angles of incidence on the 50 km layer, until a 90 km wave is returned at normal incidence. All waves longer than this will be returned at all angles of incidence. Thus we should expect low angled rays of wave-length greater than, say, 12 km to be refracted downward by the cosmic ion layer and that the long distance propagation of these wave-lengths should be governed by the layer. Since the cosmic rays are fairly uniformly distributed in direction, their ionization is constant throughout the day and night and therefore communication with waves longer than 12 km should experience no diurnal or seasonal changes. This conclusion is in good accord with observation, it being well known that wireless waves 10 km and less in length exhibit diurnal and seasonal variations and that those of length 15 km and greater show no such variations.

The foregoing agreement with the facts of long wireless waves sets an upper limit to the amount of cosmic radiation of absorption coefficient somewhat greater than $\mu = 0.25$ which can be entering the earth's atmosphere. Roughly one may say that the intensity of such radiation can not be as great as 1×10^{-4} cm^{-2} sec^{-1}. For example, suppose that a less penetrating radiation existed for which $I = 10^{-4}$ erg cm^{-2} sec^{-1} outside of the atmosphere and $\mu = 2.5$ per meter of water or $\beta = 1.2 \times 10^{-24}$. Its ionization in levels below 10 km would be too small to detect, but in levels above 40 km it, together with the ionization of Table I, would give $y = 1.2 \times 10^{4}$. λ_s would be 7 km instead of 12 km, which would be contrary to the observation that λ_s is between 10 and 15 km.

Finally, Hollingsworth[10] interpreted his experiments on interference effects of 15 km radio waves to indicate that the waves reached an effective height of 70 km, although Eckersley[10] thought that the experiments accorded better with a height of about 50 km in agreement with some results of his own.[11] These heights would agree with the curve of Fig. 1 which gives a real height of 40 to 50 km and an effective height of 50 to 70 km, the exact value depending upon the angle of incidence of the wireless ray.

5. The Nature of Cosmic Radiation

The measurements of Millikan in California, Bolivia, Canada, etc., covering magnetic latitudes from about 0 to 78°, showed that the intensity of the cosmic radiation was the same in all these places within 1%, so that at the present time the conclusion is that the intensity is constant over the earth.* Recently Epstein[12] calculated that high speed electrons from an external source impinging on the earth would be diverted by the earth's magnetic field into high latitudes; electrons of 10^9 volt energy could not hit the earth at magnetic latitudes below 58°, and of 2×10^9 volt energy below 50°. He concluded that in order to satisfy Millikan's observation of the uniform intensity of the cosmic rays over the earth the rays might be, (a) electromagnetic rays of cosmic origin, (b) corpuscular rays of higher energy than 10^9 volt, at least 6×10^{10} volt, of cosmic origin, (c) corpuscular rays of terrestrial origin. In later paragraphs we show that (c) is improbable.

We may add a remark about Epstein's conclusions. If the earth were the target of hypothetical high speed electrons of external origin, the earth would accumulate a negative charge. A charge of 7.1×10^5 coulombs would keep 10^9 volt electrons from reaching the earth; if some manner of escape of negative electricity from the earth were postulated the accumulated charge would be less. A negative charge on the earth does not disturb Epstein's analysis. To a fair approximation the electric field due to the charge would merely retard the incoming electrons, so that the 10^9 volt

[10] Hollingsworth, Jr. Inst. Elec. Eng. **64,** 579 (1926).

[11] Round, Eckersley, Tremellen and Lunnon, Jr. Inst. Elec. Eng. **63,** 933 (1925).

* Dr. Epstein kindly told me in a letter of some of Dr. Millikan's latest results at Fort Churchill, Canada.

[12] Epstein, Proc. Nat. Acad. **16,** 658 (1930).

electrons instead of hitting the earth in latitudes above 58° would be restricted to a region of still higher latitude.

According to C. T. R. Wilson,[13] in his experiments and theory of the electric field in thunder clouds, differences of potential of 10^9 volt may exist between the upper and lower portions of a thundercloud, the electric field in the cloud being downward. For a cloud 1 km thick this meant a field of 10^4 volt cm^{-1}. Since the sparking potential of dry air is around 2×10^4 volt cm^{-1}, and since thunder clouds greater than 3 km in thickness are not frequent, it is probable that the total potential difference in thunder clouds would rarely exceed 5×10^9 volt. Electrons accelerated in such a field might soon move so fast that they would experience no collisions and might finally acquire nearly the full energy of the field. They would be "run away" electrons, as he called them, and would constitute a penetrating radiation. Wilson[14] recently has suggested that run away electrons sprayed upward would describe helical paths of large radius around the lines of magnetic force and would enter the lower atmosphere at widely separated parts of the earth. This is case (c) of an earlier paragraph.

In order to examine Wilson's suggestion we use the same equations which Epstein[13] employed in his calculation. The radius of curvature ρ of the path of an electron moving normally to a uniform magnetic field of strength H is

$$\rho = mv/He(1 - v^2/c^2)^{1/2}, \tag{7}$$

where m, e and v are the rest-mass, charge and velocity of the electron, respectively, and c is the velocity of light. All quantities are in c.g.s. electromagnetic units. The energy[15] acquired by the electron in falling through a potential V is

$$Ve = mc^2(1/(1 - v^2/c^2)^{1/2} - 1). \tag{8}$$

Since v is nearly equal to c in the present problem $1/(1-v^2/c^2)^{1/2}$ is very large compared to unity and -1 may be neglected in (8). With this approximation we have from (7) and (8)

$$\rho = V/He. \tag{9}$$

These equations are strictly valid only for slowly varying velocities. However, it may be stated without giving the calculation that the classical radiation term makes a negligible correction and may be omitted.

With $V=5\times10^9$ volts, probably a maximum value, $v=c(1-5.2\times10^{-9})$, and with $H=0.5$ gauss, as at 50° magnetic latitude, ρ is 333 km. At the equator $H=0.3$ gauss, ρ is 520 km and the electron moves westward in approximately a circle of radius 520 km. Thus, keeping in mind the fact that $1/H$ and hence ρ is proportional to r^3, where r is the distance to the center of the earth, in tropical latitudes below $\pm20°$ where H is approximately horizontal the 5×10^9 volt field, mainly vertical, of the thunder cloud sprays

[13] Wilson, see Glazebrook, "Dict. of Applied Physics" **3**, 84 (1923).
[14] Wilson, Jr. Frank. Inst. **208**, 1 (1929).
[15] See Born, "Mechanics of the Atom" (1927).

the run away electrons over a region not greater than about 1000 km square to the westward.

For thunderclouds in high latitudes the electron spray is more spread out. It is difficult to calculate the distribution of the spray exactly, but an approximate idea of the distribution may be obtained. In general a thundercloud in the northern hemisphere can not spray its electrons northward, or one in the southern hemisphere southward. A northern thundercloud can, however, project its electrons southward. The magnetic line of force which touches the earth at magnetic latitude 50° rises to a maximum height of 9100 km above sea level at the magnetic equator. At this height the maximum value of ρ for the 5×10^9 volt electron is about 13,000 km, and by following out the warped helical path of the electron it is found that the electron descends to the earth in latitudes below 50°, swinging always to the westward. Therefore thunder clouds in latitude 50° spray their electrons into areas between the 50° magnetic parallels north and south, those in latitude 40° between the 40° parallels, etc., and the nearer the cloud is to the equator the more local is its run away electron spray.

Electrons ejected by 5×10^9 volt thunder clouds in higher latitudes than 50° start out approximately along the line of magnetic force and, since ρ becomes greater than r, leave the earth never to return; or at least they do so until sufficient positive charge has accumulated on the earth, 3.56×10^6 coulombs, to prevent the escape of any more electrons. After this has happened the high altitude electrons return to the earth mainly in high latitudes but it is difficult to say exactly where they will strike. However, there are relatively few thunderstorms above 50° compared to the number in lower latitudes,[16] and their electron spray will be relatively unimportant. Therefore it is concluded that the run away electron hypothesis would lead to a penetrating radiation which is most intense at low latitudes and which becomes feeble in the high latitudes. This disagrees with Millikan's observations of the constancy of the cosmic radiation with latitude. It would seem that of the various suggestions as to the nature of the cosmic rays only two are left, the rays are electromagnetic rays of cosmic origin or are very high speed electrons of cosmic origin. If the second possibility is considered the question of the charge which would accumulate on the earth must be faced.

[16] Whipple, Roy. Met. Soc. Quarterly Jr. **55**, 1 (1929).

X-RAY DIFFRACTION IN WATER: THE NATURE OF MOLECULAR ASSOCIATION

By G. W. Stewart
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(Received November 24, 1930)

Abstract

The x-ray diffraction intensity-angle distribution for water and its variation for a temperature of 2° to 98° C, are given. Two important periodicities of 3.24 and 2.11A and a third of 1.13A at 21°C are established in satisfactory agreement with Meyer. The first one *decreases* with increasing temperature and the second *increases*.

It is shown that the conception of molecular complexes explains neither the existence of these periodicities nor their change with temperature. In fact, the description of "association" that involves complexes of two or three or more molecules, should be abandoned in favor of the molecular group conception, (cybotactic condition) emphasized by the author. These groups of molecules containing hundreds and perhaps thousands of molecules in each, have a temporary existence as individuals, have ill-defined boundaries, possess an optimum size and an internal regularity determined by the temperature and molecular forces, and expand anisotropically. The experimental facts are in agreement with this view. A detailed description of the molecular arrangement in water from x-ray data is not at present possible yet it simulates the crystal arrangement in ice. A mathematical treatment of the forces within and between the molecules in such groups can probably be studied with much profit only from the quantum viewpoint.

THE nature of water has received a great deal of attention, not merely because it is the most important liquid, but because its physical properties are unusual. The present paper is not an attempt to discuss the various theories[1] concerning the constitution of water. Its purpose is to give the results of x-ray diffraction studies and to emphasize the conclusions directly toward which these studies, as well as those of other liquids, seem to point.

The examination of crystals by x-rays has shed distinctly new light upon the structure of the solid state. Its method of examination is simple and direct, being based upon both classical and quantum theories, and there seems no doubt but that the space periodicities of concentration obtained by the applications of Braggs' law is correct. During the past few years many liquids have been examined by x-ray diffraction and the conclusion is becoming increasingly strengthened that here, too, the space periodicities may be determined.[2] Indeed, these periodicities, which are clearly made evident by the diffraction experiments, seem to be caused by an approximately orderly space array of molecules in small groups having ill-defined boundaries and temporary individual existence. These groups are not sparsely distributed, but occupy the greater portion of the volume, as can be shown

[1] For a resumé see H. M. Chadwell, Chemical Reviews **4**, 375 (1927).
[2] See Stewart, Phys. Rev. **35**, 726 (1930).

by a comparison of intensity in the liquid and powdered crystal state.[3] Their magnitude appears to be of the order of hundreds or thousands of molecules, but no exact measurement has been made. The closest approach to such a measurement at present is contained in the experiments of McFarlan[4] which show that an electric field will produce increased orientation of molecules of nitrobenzene to an extent that is far greater than would be expected from the orientation of independent molecules. The effect is so small that computations should perhaps await further data.

Experimental Results

A full description of the apparatus and precautions may be found[5] in an earlier article. The Mo$K\alpha$ doublet radiation was used, being partially isolated by the use of a zirconium oxide filter. In Fig. 1 is shown an x-ray diffraction intensity-angle curve for powdered crystals of triphenylmethane. This shows, because of the comparative isolation of the line at 9°, the small amount of

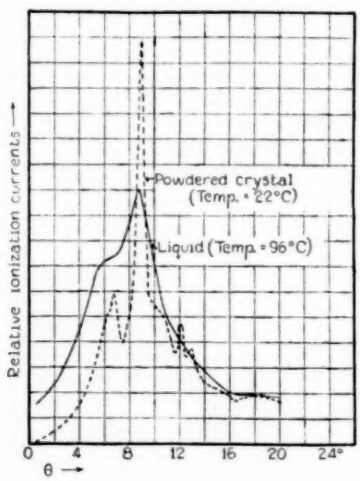

Fig. 1. X-ray diffraction curves for equal masses per unit area of triphenylmethane in liquid and powdered crystal forms.

general Mo$K\alpha$ radiation present. The general radiation is in evidence in the general elevation of the crystal curve. The maximum in the general radiation is about 6°, but the errors caused thereby, as indicated by Fig. 1 are small. A higher voltage would probably increase the general radiation to an undesirable extent. It is also to be borne in mind that the thickness of the specimen of water used was less than 1 cm or less than the optimum thickness. By this second precaution any accentuation of the general radiation by differential absorption is avoided.

[3] For example, see Fig. 1 wherein the same mass of material is used. The integral intensity in the liquid case is comparable to that of the solid.

[4] R. L. McFarlan, Phys. Rev. **35**, 12 (1930).

[5] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

Fig. 2 shows the uncorrected results of Meyer[6] by the broken line and those of the author by a continuous line. Meyer used a strictly monochromatic radiation obtained by crystal reflection. When the corrections of Meyer are made the alterations occur chiefly at the larger angles. Meyer's method was that of photography while that of the author was the ionization effect. Meyer used a stream of water and the author a thin walled glass tube as a receptacle. His monochromatic radiation gives his curve the greater quantitative weight.

Earlier diffraction experiments with water give the results presented in a foot note.[7] But none had found more than one peak until the careful work of Meyer just cited.[8]

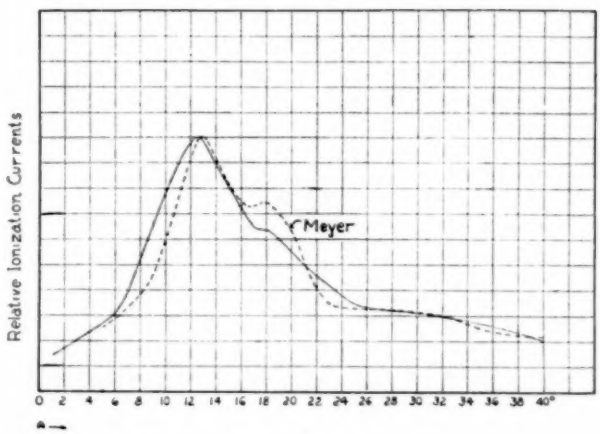

Fig. 2. Diffraction intensity of water, giving comparison of Meyer's uncorrected monochromatic curve with that of the author's. Temperatures 20° and 21°C respectively.

Fig. 3 presents the results for the change in temperature from 2° to 98°C. The tube was heated by hot (and cold) air blasts in such a manner as to prevent the introduction of any scattering material in the path of the x-rays. The temperature as given is correct to within 1.5°C throughout the entire range.

An additional experimental result must be mentioned, though it is not presented in detail because used only as a check experiment on known data. Diffraction curves were obtained with powdered ice, produced by plunging

[6] H. H. Meyer, Ann. d. Physik **5,** 701 (1930).

[7] Sogani, Ind. Jl. Physics I, **IV,** 357 (1927), has one value, 3.27A; Krishnamurti, Ind. Jl. Phys. II, **IV,** 491 (1928) has one value, 3.26A; Keesom in Physica, p. 118 (1922) and Keesom and de Smedt, Proc. Royal Soc. Amsterdam, **25,** 118 (1922) and **26,** 112 (1923) give the values 3.05A in the first two references and 3.04A in the last. Prins Zeits. f. Physik **56,** 617 (1929) gives one value, 3.1A. He raised the temperature to 80°C with no noticeable alteration.

[8] The author's experimental work preceded the publication of that of Meyer. The former was presented at the April, 1930 meeting of the American Physical Society and described by abstract only in the June 1, 1930 number of the Physical Review. Probably Meyer's article appeared in print a little later, the number of the Annalen reaching the author on July 29th, 1930, but Meyer's work was described in full at that time.

the glass tube receptacle in liquid air. The diffraction curves for two samples were in fair agreement and showed relatively prominent lines at approximately 10.5°, 11.7°, 18° and 19.5°. Dennison[9] used a Mo target and zirconium filter and found the most prominent lines to be at (1) 11.16°, (2) 19.86°, (3) 11.88° and 30.2°, (4) 15.3° and 27.16°, (5) 10.44° and 18.12° and 21.38°, the relative values being 10, 5, 2, 1.5, and 1, respectively. It will now be seen that the liquid peaks at 12.5°, 19° and 31° in Fig. 3 correspond approximately with the most intense lines found by Dennison in an extended in-

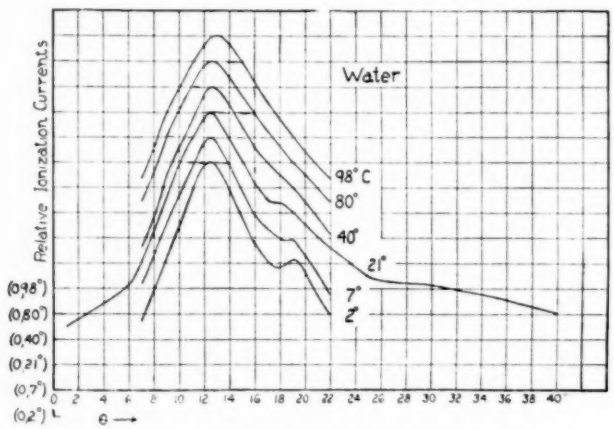

Fig. 3. Displaced diffraction intensity curves of water at different temperatures.

vestigation, and by the author in the brief tests described, in the same apparatus as was used for water. In this approximate correspondence of liquid to solid state H_2O does not differ from other compounds.[10] For example, see the liquid and crystal curves compared in Fig. 1. In case of no substance yet tried do the peaks of a liquid exactly correspond with the lines of the solid, and the difference is not a temperature one. It is evident that such periodicities as are found in the liquid state have strong quantitative similarity to the most important of those in the solid state.

Conclusions

There are several conclusions to be made directly from Fig. 3 and the foregoing assuming that Bragg's diffraction law gives the distances of separation in the periodicities represented by the peaks. Further, it is simplest to assume that these distances, 3.24, 2.11 and 1.13A, corresponding respectively to angles 12.5°, 18.8° and 31.0° of Fig. 2, or, at least the first two, correspond to molecular separations. This assumption is in accord with experiments with other liquids and with the similarity of liquid to solid state. H. H. Meyer gives as his results at 20°C, 3.13, 2.11 and 1.34A. With the assumptions cited, the conclusions are as follows:

[9] Dennison, Phys. Rev. **17,** 20 (1921).

[10] See list of eight liquids given by Krishnamurti, Ind. Jl. Phys. III, **II,** 225 (1928). The present author has tested three additional ones.

1. The distance between molecules (scattering centers) represented by the most prominent peak decreases with temperature, whereas the distance corresponding to the next most important peak seems to increase. H. H. Meyer gives a decrease for the former of 0.0018A per °C, whereas our results show 0.0014A. He obtains a constant position for the second peak.

2. The second peak disappears with increasing temperature. H. H. Meyer showed at 40°C a reduction to two-thirds the value at 3°C.

3. The breadth of the large peak increases with increase in temperature.

4. There is a quantitative similarity between the periodicities found in the liquid and the three most prominent periodicities found in powdered ice.

A few years ago the reader might have concluded at once from Fig. 3 that therein is additional evidence of the complexity of the molecules and of the disappearance of one or more complexes with increasing temperature. But the evidence of to-day would indicate at once the incorrectness of this position. For x-ray diffraction experiments indicate that when two liquids are completely miscible in the proportions used, the marked periodicity found in the solution is not that of either constituent alone, but distinctly of the solution. This has been shown by Krishnamurti[11] with glycerine, ethyl alcohol and lactic acid in an aqueous solution. Meyer[12] used solutions of n-ethyl alcohol and methyl cyclohexane, n-butyl alcohol and orthodimethyl cyclohexane, quinoline and phenol, cyclohexane and tetranitromethane and phenol and water. As an illustration of results, each of the first four mixtures used by Meyer showed but a single periodicity and this was intermediate between the periodicities of the liquids examined separately. These mixtures were totally misicble. The phenol-water mixture showed the same effect when not an emulsion. As an emulsion the two peaks of the constituents were found. The evidence shows that, without exception, two liquids, totally miscible, in solution will show a grouping of molecules (a periodicity) that is not that of either one. It is, therefore, highly probable that, if there were two "complexes" in the water in our present experiment, they would be totally miscible and would not show their individual periodicities. Hence, we may safely conclude that the two peaks in the water diffraction curve correspond to periodicities of *one kind of molecular grouping and one kind only*. The complex molecule interpretation suggested at the beginning of this paragraph is not, therefore, tenable. Moreover, it cannot be claimed that the diffraction peaks with ice indicate several complexes. They correspond to the periodicities in one molecular grouping, one crystal structure. Yet the liquid peaks have a striking similarity that is not explained by the introduction of several complexes but rather, as in ice, by periodicities in one grouping.

Langmuir[13] pointed out a number of years ago that liquids are very much more nearly like solids than like gases. Consider density, compressibility, temperature expansion, specific heats, refractive indices, other

[11] P. Krishnamurti, Ind. Jl. Physics **III,** 331 (1929).

[12] A. W. Meyer, not yet published in full; abstract, Phys. Rev. **35,** 291 (1930).

[13] Langmuir, Jl. Am. Chem. Soc. **39,** 1848 (1917).

optical properties, etc. The only essential difference between liquids and solids is that of fluidity. This one difference has had much to do with the hasty conclusion, held for many years, that the arrangements of molecules in a liquid are as irregular as in a gas. Now we learn from x-ray diffraction experiments that the liquid does have a crude regularity in multitudinous groups, an irregularity of orientation of these groups, and an irregularity of molecules between these temporary groups. With this view it would appear that the simple explanation of molecular association is the association in groups of a relatively large number of molecules and not in complexes consisting of two, three, etc., molecules. The number of molecules in a cybotactic group has not been determined, but one would expect it to be from several hundred to several thousand. Fig. 1 shows that these groups give as much scattering as powdered crystals of the same mass. The groups must therefore be practically everywhere present.

The physical chemist introduced the conception of complexes to account indirectly for the data of vapor pressure, boiling point, latent heat, viscosity, surface tension, etc.[14] But the study of crystals points very clearly to a similarity of crystal forces and internal molecular forces, and gives ample reason to expect that liquid molecules in groups as described must act differently than molecules that are more nearly free as in a gas. Consequently, what formerly has been attributed to forces between molecules in a complex are now seen to be the forces within the groups causing the regularity of arrangement.

Arrangement of molecules in the groups. In order to make the description of "association" more definite, a brief discussion will be given of the present status of the group arrangements.

The arrangement of polarized molecules is not, for example, as suggested illustratively by Debye,[15] the minimum potential configuration of two spheres (molecules) with idealized doublets of infinitesimal length at the centers, thus forming a double molecule with axes of the two doublets in line joining the centers of the spheres. Neither is the arrangement determined solely by the electrical effect of the doublets. With reference to the first point, the experiments in n-alcohols,[16] isomers of n-alcohols,[17] and normal saturated fatty acids,[18] show that when the OH or OOH group is at the end of the chain two groups are adjacent in two molecules having their chain lengths lying in the same straight line. That is, the molecules are arranged head to head (the polarized group) and tail to tail in parallel lines continuing over a group of molecules. The doublets appear at the heads and not centered in the molecule. Moreover, the head to head junction is arranged in an orderly manner with other such junctions in the adjacent parallel lines, so

[14] See Turner "Molecular Association" Longmans, Green and Co., 1915 and Longinescu, Chem. Review **4**, 381 (1929).

[15] Marx Handbook der Radiologie **VI**, 597 (1925).

[16] Stewart and Morrow, Phys. Rev. **30**, 232 (1927).

[17] Stewart and Skinner, Phys. Rev. **31**, 1, (1928).

[18] Morrow, Phys. Rev. **31**, 10 (1928).

that their location forms a definite longitudinal periodicity recognized by x-ray diffraction. The planes associated with these junctions are not normal to the chain lengths. When the polarized OH group is attached not at the end of a chain but removed therefrom by at least one carbon atom,[19] then the double arrangement disappears and the longitudinal periodicity referred to now occurs at a distance corresponding to the length of one molecule and the associated planes are normal to the chain lengths. At the same time the periodicity caused by parallel arrangement of molecules remains. It is to be noticed in the above pictures, we do not have double molecules and the association is that in a group, indeed, similar to the situation in a crystal. The original papers should be consulted for the evidence of the longitudinal grouping and the interpretation of it. So far the grouping (or association) may appear to be regarded as caused primarily by the electrical forces of the doublets. But this is not correct, for it does not account in general for the parallelism of chain molecules. A direct experiment is with n-paraffins.[20] Here the molecules lie parallel and yet they are unpolarized.[21] We are dealing with other intermolecular forces than those due to doublets. In geometric language the "shape" determines the grouping to no small extent. With the paraffins there is no periodicity in the longitudinal direction as with the n-alcohols, etc., and it is evident that this periodicity of the last named may be regarded as caused by the presence of the doublets.

The detailed arrangement of molecules in other than long chain liquid compounds is not ascertained readily by x-ray diffraction, for the lack of approximately perfect regularity in the groups makes the detectable number of periodicities too small. Thus, in the case of water no further conclusion as to detail can be made than already stated. The periodicities are evidently quantitatively similar to the most prominent ones in ice, but this does not, of course, mean like arrangement.

The above discussion states that what was formerly regarded as the peculiar association of two, three or four molecules, as the case may be, now loses its identity in the orderly group formation of molecules. If this be correct, then, since the values formerly computed for the average number of associated molecules change with temperature, there should be evidence for the alteration of the groups with temperature. This proves to be true. Skinner[22] found with a group of liquids that there were changes in the dimension of the periodicity that could not be accounted for by expansion. Similarly, in Fig. 3, it is shown that one such distance increases with temperature while the other decreases. Since neither isotropic nor anisotropic *expansion* accounts for the effect, it may be assumed that there doubtless may occur temperature changes in the molecular forces caused by alterations in molecular "shape," or essentially in the precise arrangement of atomic centers in the molecule. Skinner also showed that in certain cases the in-

[19] Stewart, Phys. Rev. **35,** 726 (1930).
[20] Stewart, Phys. Rev. **31,** 174 (1928).
[21] R. W. Dornte and C. P. Smyth, Jl. Am. Chem. Soc. **52,** 3546 (1930).
[22] Skinner, Phys. Rev. **36,** 11, 1625 (1930).

tensity of the x-ray halo *increased* with increasing temperature. This also suggests alteration in grouping.

The x-ray study is not the only experimental evidence of such internal alteration. We know, for example, that when there are changes in magnetic moment as occurs, for example, in para-azoxyanisol, there must be internal changes in the molecule.

The group conception, as given above, seems to be in harmony with all the facts. On the other hand, there are good reasons for the abandonment of the theory of complexes. Reference to a recent contribution of G. G. Longinescu,[23] who has been an active contributor in this field, will satisfy the reader upon this point. The most important reason for turning from the older conception is that it has proved unprofitable and does not longer serve any useful purpose in stimulating new contributions. Its extended use has increased the inconsistent results and it has ceased to be even empirically satisfactory.

The new conception here proposed seems to be helpful in several respects. First, it suggests that experiments based upon the theory of complexes will not prove profitable and recommends their abandonment. Second, it states that the secret of association lies in an understanding of those forces, call them chemical or physical as one will, which bind atoms together in a molecule and which cause stable configuration in crystals and unstable arrangement in liquids. If, as at present appears, such an "understanding" will only be had through the development of quantum theory, these forces being studied by the energy levels obtained in radiation and absorption spectra of constituent atoms and molecules, then a physical description of the origin of these forces appears improbable. They will appear to exist only because of atomic and molecular energy levels,[24] and the resulting energy changes. They cannot be understood by distributions of electricity and the application of electrical laws. That has proved unsatisfactory even for the simplest atoms. In any event, the cybotactic group conception of association removes the difficulties inherent in molecular complexes and will prove helpful in a study of the nature of the liquid state.

I desire to express appreciation for the experimental skill of Mr. H. A. Zahl, research assistant, who is responsible for the observations involved in this report, and thanks for a supply of conductivity water to Professor J. N. Pearce of this University.

[23] Longinescu, Chemical Review **6**, 381 (1929). See also J. W. Williams, Chemical Review **6**, 589 (1929) and particularly p. 614 *et. seq.*

[24] See Langer, Phys. Rev. **34**, 92 (1929).

ON THE TRANSFORMATION OF LIGHT INTO HEAT IN SOLIDS. I[1]

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Abstract

Starting from the analogy between a crystal and molecule, it is shown that the electronic excitation, forming the first step in the process of light absorption, is not confined to a particular atom, but is diluted between all of them in the form of "excitation waves," similar to sound waves which are used to describe the heat motion in the same crystal. Owing to the interaction between the atoms the excitation state is split up into substates whose number is equal to the number of atoms n (excitation multiplet). By superposing several excitation waves "excitation packets" can be constructed representing the travelling of the excitation state from one atom to another. To each excitation sub-state there corresponds a definite crystal structure (lattice constant, vibration frequencies) slightly different from that of the normal, and giving rise to slightly different vibrational states. This influence of the excitation on the vibrational states provides an indirect coupling between them, which allows the excitation energy to be shared between a few hundred heat-oscillators with practically no direct coupling nor anharmonicity in a radiationless transition which forms the second state of the process of light absorption.

1. Introduction

In a monatomic gas the transformation of the light energy absorbed by an individual atom into heat, that is into the kinetic energy of the translatory motion, is effected, on the quantum theory, through *a collision of the second kind* of the excited atom with some other (usually unexcited) one. If we now look for the corresponding process in a monatomic solid body, where the heat motion is represented by the vibration of a set of "elastic oscillators" (Debye's waves), we at once meet a grave difficulty. This difficulty consists in the apparent inability of the elastic or heat oscillators, so far as they are assumed to be harmonic and uncoupled with each other, to take up the big quantum of energy stored by the excited atom. This quantum is in fact about 100 times larger than the largest energy quantum of the heat oscillators, corresponding to the ratio between the frequency of the absorbed light and the highest frequency of the heat vibrations. In a radiationless discharge of the excitation energy the latter must therefore be either shared between a great many oscillators, which is impossible if they are uncoupled, or be absorbed by a single oscillator jumping at one time over at least 100 energy levels, which is also impossible if the oscillator is harmonic.

The solution of this difficulty seems at first sight to consist simply in taking account of the actually existing coupling between the different oscil-

[1] This paper is an extension of two previous ones on the absorption of light in gases: see J. Frenkel, Zeits. f. Physik **58**, 798 (1929) and **59**, 198 (1930).

lators and their nonharmonic character. It must, however, be rejected for it leads to extremely small probabilities for transitions of the type considered. In fact in order to get a non-vanishing probability for a transition involving N elementary jumps, either by N oscillators making each an elementary jump, or by a single oscillator making an N-fold jump, one must carry out the expansion of the potential energy of the oscillators as a function of their coordinates (or of the displacements of the atoms from their equilibrium positions) up to terms of the N-th order at least.[2] The terms one would get for $N \leqq 100$, even if this was practicable, would be hardly large enough to account for the effect we are considering.

There seems to be a less trivial and more successful solution of the above difficulty, which is suggested *by the analogy between a crystal (representing a solid body) and a molecule.* The usual selection rule for the vibrational quantum number of a molecule (a diatomic molecule, say), restricting its change to unity, holds for such transitions only, for which the electronic state of the molecule remains unaltered. In case however of a combined transition, for instance of a spontaneous transition from an excited state to the normal one with emission of light, the vibrational quantum number can change by any amount (integral, of course) whatever. It may be noted that this "breach" of the selection rule has nothing to do with the possible presence of nonharmonicity, but depends upon the fact that the character of the vibrations in the normal and excited molecule is quite different.

In applying this consideration to a crystal we have only to develop the analogy between an excited crystal and an excited molecule. At the outset we have pictured an excited crystal as differing from the normal one by the presence of one *definite* excited atom. Now in case of a molecule consisting of two identical atoms the excitation cannot be traced to one of them, but has to be considered as a characteristic of the molecule as a whole. The same must be true with respect to a crystal consisting of any number of identical atoms. We thus see that we must first of all revise our conception of an excited crystal by allowing for the identity of all the atoms, and thereafter investigate the influence of the "electronic state" of a crystal on its vibrational states.

2. Excited States of a Crystal; "Excitation-Waves"

We shall assume that the coupling between different—even neighboring—atoms is small compared with the forces holding the electrons within the separate atoms (thus excluding the case of metallic bodies). We shall further suppose that the atoms—or rather the nuclei—are fixed, that is, we shall neglect their vibratory motion, and shall consider only their inner state, characterized by a function of the coordinates of the electrons with respect to the nucleus. Lastly we shall leave out of account the possibility of interchanging the electrons between different atoms and shall consequently assign to a definite atom a definite group of electrons whose coordinates (relative

[2] See below, Section 4.

to the nucleus) will be represented for the sake of brevity by the number of the respective atom $(1, 2, \cdots, n)$.

Then if ψ_{I} and ψ_{II} are the wave functions representing the normal and the excited state of an *isolated* atom, the stationary states of a system of n atoms, of which one is excited and the rest normal, will be represented to a first approximation by a linear aggregate of n factorial functions,

$$\begin{aligned}
\phi_1 &= \psi_{\mathrm{II}}(1)\psi_{\mathrm{I}}(2)\psi_{\mathrm{I}}(3)\cdots\psi_{\mathrm{I}}(n)\\
\phi_2 &= \psi_{\mathrm{I}}(1)\psi_{\mathrm{II}}(2)\psi_{\mathrm{I}}(3)\cdots\psi_{\mathrm{I}}(n)\\
&\cdots\cdots\cdots\cdots\\
\phi_n &= \psi_{\mathrm{I}}(1)\psi_{\mathrm{I}}(2)\psi_{\mathrm{I}}(3)\cdots\psi_{\mathrm{II}}(n)
\end{aligned} \tag{1}$$

with properly chosen coefficients $c_1, c_2, \cdots, c_n$. We have here a particular case of an "exchange degeneracy," which I have already considered previously[3] and which is somewhat similar to the exchange degeneracy met with in the problem of a single electron with n fixed identical nuclei.[4]

There are, as is well known, just n *sets* of coefficients $(c_1, c_2, \cdots, c_n)$, corresponding to the splitting up of the undisturbed state of n isolated atoms with the total energy $W_{\mathrm{II}}+(n-1)W_{\mathrm{I}}$ into n different states, whose energies differ from the preceding value by small amounts W'. These n states will be denoted as the "excitation multiplet" of the crystal. The values of W' for the different components of such a multiplet "$W'=W_r'$) and the corresponding values of the coefficients $c_l(=c_{rl})$ are determined by the equations

$$\sum_{l=1}^{n} U_{kl}c_l = W'c_k \tag{2}$$

where U_{kl} are the matrix elements of the mutual potential energy of all the atoms U with respect to the functions (1).

Now U must reduce to the form

$$U = \sum_{\alpha<\beta} U(\alpha, \beta; R_{\alpha\beta}) \tag{3}$$

where $U(\alpha, \beta; R_{\alpha\beta})$ is the mutual potential energy of the atoms α and β and $R_{\alpha\beta}=R_{\beta\alpha}$ their distance apart (or rather the distance between the respective nuclei). One has obviously $U(\alpha, \beta; R_{\alpha\beta})=U(\beta, \alpha; R_{\alpha\beta})$. One must not conclude however from this symmetry relation that $U(1, 2, \cdots, n)$ is a symmetrical function of the respective arguments. Interchanging two arguments say 1 and 2—which corresponds eventually to an interchange of the excitation state between the atoms 1 and 2—*we must keep the distances $R_{\alpha\beta}$ fixed*, so that the new energy function obtained by such an interchange is substantially different from the original one.[5]

[3] Zur Theorie der Resonanzverbreiterung von Spektrallinien, Zeits. f. Physik **59**, 198 (1930).

[4] This problem is treated in Bloch's theory of metallic conductivity.

[5] The theory can be easily extended to account for the interchanging of the electrons between different atoms. In the simplest case of one electron per atom we have but to replace

Taking into account the orthogonality and normality conditions for the functions ψ_{I} and ψ_{II},

$$\int \psi_{\mathrm{I}}(\alpha)\psi_{\mathrm{II}}^{*}(\alpha)d\tau_{\alpha} = 0, \quad \int \psi_{\mathrm{I}}(\alpha)\psi_{\mathrm{I}}^{*}(\alpha)d\tau_{\alpha} = \int \psi_{\mathrm{II}}(\alpha)\psi_{\mathrm{II}}^{*}(\alpha)d\tau_{\alpha} = 1,$$

we easily obtain from (3) if $k \neq l$:

$$U_{kl} = \int \cdots \int U\phi_k^{*}\phi_l \; d\tau_1 \cdots d\tau_n = V_{kl} \tag{4}$$

where V_{kl} is a *function of the distance* R_{kl} *alone* given by

$$V_{kl} = \int\int U(k, l; R_{kl})\psi_{\mathrm{II}}^{*}(k)\psi_{\mathrm{I}}(k)\psi_{\mathrm{I}}^{*}(l)\psi_{\mathrm{II}}(l)d\tau_k d\tau_l \tag{4a}$$

It may be remarked that it is in general complex and therefore different from $V_{lk} = V_{kl}^{*}$.

For $k = l$ we get

$$U_{kk} \equiv V_{kk} = \sum_{l \neq k} \overline{V}_{kl} \tag{5}$$

where

$$\overline{V}_{kl} = \int\int U(k, l; R_{kl}) \left| \psi_{\mathrm{II}}(k) \right|^{2} \left| \psi_{\mathrm{I}}(l) \right|^{2} d\tau_k d\tau_l \tag{5a}$$

may be defined as the average value of the mutual energy of the atoms k and l when one of them is in the normal and the other in the excited state. This is also of course a function of the distance R_{kl} only; it is moreover symmetrical with respect to k and l.

The equations (2) are very similar to those which determine the normal modes of vibration of a system of coupled classical oscillators with one degree of freedom each; in fact we have but to consider the coefficients c_k as the amplitudes of these oscillators and to replace the energies W' by the square of the classical frequencies (multiplied by a properly chosen proportionality factor). The matrix elements $U_{kl}(k \neq l)$ can be then interpreted as the coupling coefficients (since they actually depend upon the distance of the

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the functions (1) by the following ones which are antisymmetrical with respect to all the electrons.

$$\phi_1 = \frac{1}{n!^{1/2}} \begin{vmatrix} \psi_{\mathrm{II}}(1,1), & \psi_{\mathrm{II}}(1,2), \cdots \psi_{\mathrm{II}}(1,n) \\ \psi_{\mathrm{I}}(2,1), & \psi_{\mathrm{I}}(2,2), \cdots \psi_{\mathrm{I}}(2,n) \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \psi_{\mathrm{I}}(n,1), & \psi_{\mathrm{I}}(n,2) \cdots \psi_{\mathrm{I}}(n,n) \end{vmatrix} \cdot \quad \phi_2 = \frac{1}{n!^{1/2}} \begin{vmatrix} \psi_{\mathrm{I}}(1,1), & \psi_{\mathrm{I}}(1,2) \cdots \psi_{\mathrm{I}}(1,n) \\ \psi_{\mathrm{II}}(2,1), & \psi_{\mathrm{II}}(2,2) \cdots \psi_{\mathrm{II}}(2,n) \\ \cdots\cdots\cdots\cdots\cdots\cdots \\ \psi_{\mathrm{I}}(n,1), & \psi_{\mathrm{I}}(n,2) \cdots \psi_{\mathrm{I}}(n,n) \end{vmatrix}$$

etc. where $\psi_{\mathrm{I}}(k, l)$ and $\psi_{\mathrm{II}}(k, l)$ denote the wave functions of the atom formed by the association of the l-th electron to the k-th nucleus, in the normal and excited state respectively. Similar, though somewhat more complicated, results are obtained in the general case of several electrons per atom.

The case of two electrons with all the atoms being in the normal state has been recently treated by E. Hylleraas, Zeits. f. Physik **63**, 771 (1930) in connection with the theory of the cohesive forces in a (non-excited) crystal of sodium hydride.

respective oscillators only), and the U_{kk} as the coefficients of the quasi-elastic forces for the uncoupled oscillators.

Until now the positions of the atoms have remained unspecified. We shall now assume that the nuclei are fixed at the lattice points of the crystal, neglecting the displacements due to the vibratory motion. We shall further assume that the crystal has a rectangular form (or the form of a parallelepiped whose edges are parallel to the crystalline axes). The normal modes of vibration for this case are well known. They do not depend upon the shape of the functions $V_{kl}(R_{kl})$ nor upon the value of the constant $V_0 = V_{kk}$, thus coinciding with respect to the position of the nodal planes with the acoustic or elastic vibrations (for which $V_0 = 0$). These vibrations can be described as *standing waves* with the wave-number components[6]

$$g_1 = \pm\, r_1/2a_1,\quad g_2 = \pm\, r_2/2a_2,\quad g_3 = \pm\, r_3/2a_3 \tag{6}$$

where a_1, a_2, a_3 are the edges of the crystal and r_1, r_2, r_3 numbers specifying the mode of normal vibrations and taking all integral values between 0 and n_1-1, n_2-1, n_3-1, respectively, n_i being the number of atoms along the i-th edged ($n = n_1 n_2 n_3$).

The triplet $(r_1 r_2 r_3)$ replaces the number r which was introduced to specify the various solutions of the equations (2). The single numbers k and l must be replaced accordingly by triplets $(k_1 k_2 k_3)$, $(l_1 l_2 l_3)$ which may be associated with definite "oscillators," that is definite atoms of the lattice. It may be remarked that the coefficient c_k in (2) refers to that function ϕ_k in (1) which ascribes the excited state to the atom k. The solutions of the equations (2) can now be put in the form

$$c_{r_1,r_2,r_3;k_1,k_2,k_3} = A_{r_1 r_2 r_3} \cos\frac{\pi\delta}{a_1} k_1 r_1 \cos\frac{\pi\delta}{a_2} k_2 r_2 \cos\frac{\pi\delta}{a_3} k_3 r_3 \tag{7}$$

where δ is the lattice constant (for the sake of simplicity the lattice will be pictured as cubical), and $k_1\delta = x_1$, $k_2\delta = x_2$, $k_3\delta = x_3$ the rectangular coordinates of the atom to which the excited state is assigned by the function $\phi_{k_1 k_2 k_3}$. $A_{r_1 r_2 r_3}$ is a normalization coefficient determined by the condition that the integral of the square of the function

$$\chi_{r_1 r_2 r_3}(1, 2, \cdots n) = \sum_{k_1 k_2 k_3} c_{r_1,r_2,r_3;k_1,k_2,k_3} \phi_{k_1 k_2 k_3}(1, 2, \cdots n) \tag{7a}$$

representing the r-th stationary state of the excited crystal (the r_1, r_2, r_3 component of the "excitation multiplet") over the configuration space of all the electrons should be equal to 1.

The energies $W'_{r_1 r_2 r_3}$ of the different states (with respect to the unperturbed energy $W_{II} + (n-1)W_I$) are given directly by substituting in the equations (2) the values (7) of the coefficients c. Since the matrix elements U_{kl} depend only upon the differences $k_1 - l_1$, $k_2 - l_2$, $k_3 - l_3$ one can put $k_1 = k_2 = k_3 = 0$ which gives

$$A_r W'_r = \sum_l U_{0l} c_{rl}$$

[6] The wave number is the reciproal of the wave-length; it is a vector parallel to the direction of the propagation of the waves.

or more fully written

$$W'_{r_1r_2r_3} = \sum_{l_1} \sum_{l_2} \sum_{l_3} U_{000,l_1l_2l_3} \cos \frac{\pi\delta}{a_1} l_1 r_1 \cos \frac{\pi\delta}{a_2} l_2 r_2 \cos \frac{\pi\delta}{a_3} l_3 r_3 \qquad (8)$$

With increasing values of $l_1l_2l_3$, that is with increassing distance $R_{0l} = \delta(l_1^2 + l_2^2 + l_3^2)^{1/2}$, the values of $H'_{000l_1l_2l_3}$ must in general decrease very rapidy. The summation in (8) can be therefore extended practically over all values of the l_i from $-\infty$ to $+\infty$. If the mutual action of neighboring atoms only (with smallest distance apart $R = \delta$) is taken into account, (8) reduces to

$$W'_{r_1r_2r_3} = V_0 + 2V_1\left(\cos \frac{\pi\delta}{a_1} r_1 + \cos \frac{\pi\delta}{a_2} r_2 + \cos \frac{\pi\delta}{a_3} r_3\right) \qquad (8a)$$

where V_1 is the value of (4a) for neighboring atoms and V_0 six times the value of (5a) for the same atoms. The latter value is the average of the mutual potential energy between an excited and an unexcited atom, whereas V_1 has the character of an "exchange energy" which has no classical analogue.

Each stationary state of an excited crystal can be described as a "standing excitation wave" defined by (7) or by

$$c(x_1x_2x_3) = A \cos 2\pi g_1 x_1 \cos 2\pi g_2 x_2 \cos 2\pi g_3 x_3 e^{-2\pi i\nu' t}$$

where $\nu' = W'_r/h$, $x_i = \delta l_i$. Such a standing wave can be obtained by superposing eight "progressive excitation waves" of the type

$$(A/8)e^{2\pi i(g_1x_1 + g_2x_2 + g_3x_3 - \nu' t)}$$

which represent the propagation of the probability for finding the excitation localized in a certain plane of the crystal. By superposing a number of such waves with slightly different values of g_1, g_2, g_3 (that is with slightly different directions of propagation and frequencies $\nu' = w'/h$) it is always possible to construct a wave-packet which will represent the excitation being concentrated in a definite atom or its neighborhood (according to the usual picture). The group velocity of such an "excitation-packet" may be determined by the relations

$$v_i = \partial\nu'/\partial g_i (i = 1, 2, 3). \qquad (9)$$

Putting

$$h\nu' = V_0 + 2V_1(\cos 2\pi g_1\delta + \cos 2\pi g_2\delta + \cos 2\pi g_3\delta)$$

according to (8a) and (6), we get

$$v_i = -\frac{4\pi\delta V_1}{h} \sin 2\pi g_i\delta. \qquad (9a)$$

For small values of g_i that is for long "excitation waves" this expression reduces to

$$v = -\frac{8\pi^2\delta^2 V_1}{h} g \qquad (9b)$$

that is the group velocity is approximately proportional to the wave number. It has in general the same direction so long as the "exchange energy" V_1 is negative. It reaches its maximum value $v \leqq 4\pi\delta \left| V_1 \right| /h$ for wave-lengths equal approximately to four times the interatomic distance δ. For $\lambda \leqq 2\delta$ it falls down to zero and for still shorter wave-lengths becomes opposite to the direction of the wave propagation.[7]

To get a better understanding of the nature of the "excitation waves" it will be well to consider the process corresponding to them in the older quantum theory and in the classical theory. According to the former the exitation energy of an atom can and in fact must be transmitted to one of the other atoms of the same sort either by emission and (resonance) reabsorption, of light or directly in a non-radiative process. The closer the atoms are together, the larger must be the probability of such a non-radiative transmission, that is, the larger the velocity with which the "excited state" will travel from one place to the other. This is expressed by the fact that the group velocity, according to (9a), is proportional to the exchange energy V_1. The ratio $\delta/v_{\max}$ which is of the order of magnitude of h/V_1 can be considered as the shortest time that the excitation remains confined to one definite atom.[8]

From the point of view of the classical theory an atom has to be considered as a harmonic oscillator, whose normal state is that of rest. The energy of the free oscillations, replacing the excitation energy, instead of being concentrated in one single atom (or a small number of them in the general case) has to be distributed here in a more or less uniform manner over all the atoms, each of them possessing accordingly but a very small energy. The excitation waves can be represented in this case by the familiar waves of the electric polarization with exactly the same wave-numbers as has been actually done above in the discussion of the equation (2).[9] It should be noticed however that in the classical theory of the propagation of such waves the interaction between the atoms is considered to be a radiative one, that is proportional to their dipole moment and inversely proportional to the distance, whereas in the wave mechanical theory we are developing this interaction considered as a much more powerful non-radiative (electrostatic) one.[10]

[7] These results are wholly analogous to those implied in Bloch's theory of the electrical conductivity of metals and discussed by R. Peierls.

[8] In case of two atoms h/V_1 is just equal to the time in which the excited state oscillates from one atom to the other.

[9] The situation becomes more complicated if instead of one excited atom we consider the case of two or more excited atoms. cf. J. Frenkel, Zeits. f. Physik **59**, 198 (1930) in particular footnote on p. 203.

[10] Cf. G. Breit and E. O. Salant, Phys. Rev. **36**, 871 (1930). This paper dealing with the propagation of light in solids contains some results of the present section.

3. The Influence of Excitation on the Geometric and Elastic Properties of a Crystal and its Vibratory Motion

We can now turn to the examination of the influence which an excited state of a crystal (that is a definite component of an excitation multiplet) exerts upon the heretofore neglected vibratory motion of the atoms. The exact way to deal with this question would be to consider simultaneously the "inner" and the "outer" (that is, vibratory) motion of the atoms. But this way is hardly practicable even in the simplest case of a diatomic molecule, and we shall therefore use an approximate method of the same sort which is applied in Debye's theory of specific heats to the determination of the normal vibrations corresponding to the unexcited state.

A normal vibration is described here by a system of standing sound waves of just the same geometrical type as that used in the preceding paragraph to describe the excitation states. It can be thus characterized by specifying the components of the wave-number according to the equations (6) which we shall rewrite in the form

$$g_1' = \pm r_1'/2a_1, \quad g_2' = \pm r_2'/2a_2, \quad g_3' = \pm r_3'/2a_3 \tag{10}$$

the primes serving to distinguish the sound waves from the excitation waves.[11]

The frequency of the vibrations ν' can be determined from the equation

$$\nu' = g'u \tag{11}$$

where u denotes the *velocity of sound*, which is considered as independent of g'. The velocity of sound can be calculated by means of the formula

$$u = (\kappa/\rho)^{1/2}$$

where ρ is the density of the crystal, and κ its elastic modulus, which has different values for the longitudinal and the transverse vibrations.

Now in order to determine κ from atomic data we must consider the vibrationless state of the crystal and compare its energy in the equilibrium state with the energy corresponding to a slightly compressed (or expanded) state in the case of κ_{long} or to a slightly distorted state in the case of κ_{trans}.

Denoting the volume of the crystal with v and its energy—that is the mutual potential energy of all its atoms—in the normal (non-excited) state with W_0 we have, expanding W_0 in a power series with respect to the increment of volume $v-v^0$ ($v^0=v$ in the equilibrium state)

$$W_0 = W_0{}^0 + \frac{1}{2}\left(\frac{\partial^2 W_0}{\partial v^2}\right)^0 (v - v^0)^2.$$

The second term represents the elastic energy

$$\tfrac{1}{2}\,\kappa_0(v-v^0)^2 \cdot v^0$$

[11] We shall drop the primes later on when there will be no danger of confusing the sound waves with the excitation waves.

whence it follows

$$\kappa_0 = v_0{}^0\left(\frac{\partial^2 W_0}{\partial v^2}\right)$$

or putting $v = n\delta^3$

$$\kappa_0 = \frac{\delta_0{}^2}{9}\,\frac{1}{v_0{}^0}\left(\frac{\partial^2 W_0}{\partial \delta^2}\right)^0 = \frac{1}{9n\delta_0}\left(\frac{\partial^2 W_0}{\partial \delta^2}\right)^0. \tag{13}$$

This formula determines the modulus of compressibility for the normal (unexcited) state of the crystal—as denoted by the subscript zero—and hence according to (12) and (11)[12] the frequency of the vibrations associated with this state. It may be remarked that the corresponding equilibrium value of $\delta = \delta_0{}^0 = \delta_0$ is given by the equation $(\partial W_0/\partial v)^0 = 0$ or

$$(\partial W_0/\partial \delta)^0 = 0 \tag{13a}$$

and that δ_0 is related to the density $\rho = \rho_0$ by means of

$$\rho_0 = m/\delta_0{}^3 \tag{13b}$$

m being the mass of an atom.

The above method can now obviously be applied to the determination of the vibrations associated with an excited state of the crystal. To do this we have but to replace in the preceding formulae the energy W_0 by the energy $W_r = W_0 + W'_r$ of one of the components of the excitation multiplet. In this way we shall get for the lattice constant of the crystal δ_r its density ρ_r and its elastic modulus κ_r values depending upon the character of the excitation substate and slightly different from those corresponding to the normal one.

Since the difference $\delta_r - \delta_0 = \Delta\delta_r$ is very small, we have to a first approximation

$$\left(\frac{\partial W_r}{\partial \delta_r}\right)^0 = \left(\frac{\partial W_0}{\partial \delta}\right)_{\delta=\delta_0} + \left(\frac{\partial^2 W_0}{\partial \delta^2}\right)_{\delta=\delta_0}\Delta\delta_r + \left(\frac{\partial W_r'}{\partial \delta}\right)_{\delta=\delta_0} = 0,$$

whence since the first term vanishes (according to 13a)

$$\Delta\delta_r = -\frac{\partial W_r'}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2}\ (\delta = \delta_0) \tag{14}$$

The energy W_0 is proportional to the number of atoms n, whereas W'_r according to (8) or (8a) depends upon it in a practically unimportant way. Putting in (8a)

$$a_1 = n_1\delta,\quad a_2 = n_2\delta,\quad a_3 = n_3\delta$$

(where $n_1 n_2 n_3 = n$) we have

$$W_r' = V_0 + 2V_1\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r_3}{n_3}\right) \tag{15}$$

and consequently

$$\Delta\delta_r = -\frac{\partial V_0}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2} - 2\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r^3}{n_3}\right)\frac{\partial V_1}{\partial \delta}\Big/\frac{\partial^2 W_0}{\partial \delta^2} \tag{15a}$$

which is of the order of magnitude of $1/n$, since V_1 does not depend upon n.

[12] In the case of longitudinal vibrations.

In the same way we get from (13)

$$\Delta\kappa_r = \kappa_r - \kappa_0 = \frac{2}{9\delta n}\left[\frac{\partial^2 V_0}{\partial\delta^2} + 2\left(\cos\frac{\pi r_1}{n_1} + \cos\frac{\pi r_2}{n_2} + \cos\frac{\pi r_3}{n_3}\right)\right]\frac{\partial^2 V_1}{\partial\delta^2}\cdot \quad (15b)$$

The relative change of $\Delta\kappa_r$ being again of the order of magnitude of $1/n$.

These results seem very natural indeed. We should expect that the change of the geometric and dynamic properties of the crystal lattice, due to the excitation of a few atoms n' depends upon their *relative* number, that is upon the ratio n'/n, which in our case is equal to $1/n$. So long as n' is small compared with n the effects due to the excitation of the separate atoms must obviously behave additively (which would no longer be the case if n' were comparable with n), so that to get the total change of δ or κ we would have but to add the expressions (15a) or (15b) for all the n' excited atoms. It seems however that even with the largest values of n' that can be obtained by illuminating the crystal with intense light of the resonance frequency, the change in the elastic properties will be too minute to be detected by direct measurement.

This change must however manifest itself in an indirect manner by making possible the radiationless transitions of the crystal from an excited state into the normal one with conversion of the excitation energy into that of the vibrational motion, and also of course transitions of the inverse direction, leading to "thermal excitation" of the crystal and corresponding to "inelastic collisions of the first kind" or "activating collisions" in the case of a gas.

4. The Relation between the Variables and Functions describing the Heat Oscillators in the Normal and the Excited Crystal

In order to determine the probability of such transitions we must introduce first of all the "normal coordinates" characterizing the individual heat oscillators, which represent the different modes of vibration (standing elastic waves) of the crystal. Let these coordinates for the unexcited state be denoted by $\xi_1, \xi_2, \cdots \xi_n \cdots \xi_{3n}$ (their number being equal to the number of degrees of freedom); we shall think of the first n as referring to the longitudinal vibrations and the rest to transverse ones.

We have to introduce in the second place the relations between these coordinates and the normal coordinates $\xi_{r1}, \xi_{r2}, \cdots$ which correspond to the r-th excited state. These relations must be derived from the condition that the equilibrium positions of the atoms in the excited state are specified by zero values of the new coordinates ($\xi_{rs} = 0$) on the one hand and by definite non-vanishing values $\xi_s = \xi_s^r$ of the old ones on the other.

For the sake of simplicity we shall limit ourselves to the consideration of a *unidimensional* case, that is of a set of n atoms situated on a straight line and capable of moving along this line (that is to perform longitudinal oscillations). Such a set can be conveniently treated as a "bar." In order to allow for the change of length $L = \delta n$ of the bar, due to the excitation of one of its

atoms we shall imagine one of its ends to be fixed and the other free.[13] The normal modes of vibration of such a bar correspond to wave-lengths $\lambda=\lambda_l$ determined by the equation

$$L = \frac{2l+1}{4}\lambda_l = n\delta \tag{16}$$

where $l=0, 1, 2, \cdots n-1$. The displacement Δx_k of an atom whose equilibrium distance from the fixed end is $x_k=k\delta$ can be represented by the sum

$$\Delta x_k = \sum_{l=0}^{n-1} c_{kl}\xi_l \tag{17}$$

where

$$c_{kl} = \gamma \sin\frac{2\pi x_k}{\lambda_l} = \gamma \sin\frac{\pi}{n}\left(l+\frac{1}{2}\right)k \tag{17a}$$

γ being determined by the "normality condition"

$$\sum_{k=0}^{n-1} c_{kl}^2 = 1 \tag{17b}$$

and ξ_l denoting the normal coordinate, which characterizes the l-th mode of vibration.

Using the formula

$$\sum_{k=0}^{n-1} e^{i\alpha k} = \sum_{k=0}^{n-1}\cos\alpha k + i\sum_{k=0}^{n-1}\sin\alpha k = \frac{1-e^{i\alpha n}}{1-e^{i\alpha}}$$

which is equivalent to

$$\sum_{k=0}^{n-1}\operatorname{cs}\alpha k = \frac{1+\cos\alpha(n-1)-\operatorname{cs}\alpha n-\operatorname{cs}\alpha}{2(1-\operatorname{cs}\alpha)} = \frac{1}{2}(1-\operatorname{cs}\alpha n) + \frac{\operatorname{sn}\alpha n\,\operatorname{sn}\alpha}{2(1-\operatorname{cs}\alpha)}$$

$$\sum_{k=0}^{n-1}\operatorname{sn}\alpha k = \frac{\sin\alpha(n-1)-\sin\alpha n+\sin\alpha}{2(1-\operatorname{cs}\alpha)} = -\frac{1}{2}\sin\alpha n + \frac{\operatorname{sn}\alpha(1-\operatorname{cs}\alpha n)}{2(1-\operatorname{cs}\alpha)},$$

we get with the abbreviations $(l+\frac{1}{2})\pi/n=\beta$, $(l'+\frac{1}{2})\pi/n=\beta'$

$$\sum_{k=0}^{n-1} c_{kl}c_{kl'} = \gamma^2\sum_{k=0}^{n-1}\sin\beta k\sin\beta' k = \frac{1}{2}\gamma^2\left[\sum_{k=0}^{n-1}\operatorname{cs}(\beta-\beta')k - \sum_{k=0}^{n-1}\operatorname{cs}(\beta+\beta')k\right]$$

$$= n-1 \text{ if } l'=l \text{ and } (-1)^{l\pm l'+1} \text{ if } l'=l.$$

We thus see that

$$\gamma = (n-1)^{-1/2}$$

and morever that the coordinates ξ_l are *not exactly* orthogonal as they would be in the limiting case $n\to\infty$, $n\delta=L=\text{const.}$

[13] Similar results would be obtained by fixing the middle point of the bar and leaving both ends free and in the opposite phase.

Squaring (17) and summing up with respect to k we have in fact:

$$\sum_{k=0}^{n-1}(\Delta x_k)^2 = \sum_{l=0}^{n-1}\xi_l^2 - \frac{2}{n-1}\sum_{l<l'}(-1)^{l'-l}\xi_l\xi_{l'}.$$

The mutual potential energy of the atoms which in the simplest case is represented by the sum

$$\sum_{k=0}^{n-2}(\Delta x_{k+1} - \Delta x_k)^2$$

also will not be reduced exactly to a sum of squares of the type

$$2\pi^2\sum_{l=0}^{n-1}\nu_l^2\cdot\xi_l^2$$

ν_l being the vibration frequencies, but will contain cross terms vanishing in the limiting case of a continuous bar. The problem of finding the exact normal coordinates that is the exact transformation coefficients c_{kl} in the equations (17) for a given finite value of n is rather complicated and we shall therefore use the "nearly-normal" coordinates defined above.

Since the coefficients c_{kl} do not depend upon the equilibrium spacing between the atoms δ, the same formulae (17) could be used both for the "normal" and for the "excited" bar; it should be remembered however that Δx_k has in both cases a different meaning, the equilibrium position of the k-th atom in the excited state being displaced by $\Delta\delta_r k$ with respect to that corresponding to the normal state. The same position of the atoms which in the normal state is specified by the displacements (17) will be specified from the point of view of the excited state r by the displacements

$$\Delta x_{rk} = \Delta x_k - k\Delta\delta_r = \sum c_{kl}\xi_{rl}$$

whence

$$\sum_{l=0}^{n-1}c_{kl}(\xi_{rl} - \xi_l) = -k\Delta\delta_r.$$

If c_{kl} were the correct transformation coefficients then these equations would be immediately solved by

$$\xi_{rl} - \xi_l = \Delta\xi_{rl} = -\sum_{k=0}^{n-1}c_{kl}k\Delta\delta_r.$$

Introducing here the approximate values

$$c_{kl} = \frac{1}{(n-1)^{1/2}}\sin\frac{\pi}{n}\left(l + \frac{1}{2}\right)k$$

we have

$$\Delta\xi_{rl} = -\frac{\Delta\delta_r}{(n-1)^{1/2}}\sum_{k=0}^{n-1}k\sin\alpha k$$

or

$$\Delta\xi_{rl} \leqq \frac{\Delta\delta_r}{n^{1/2}}\left(\frac{\partial}{\partial\alpha}\sum_{k=0}^{n-1}\cos\alpha k\right)_{\alpha=\pi/n(l+1/2)}$$

that is according to the summation formula given above, with $\cos \alpha n = 0$, $\sin \alpha n = (-1)^l$,

$$\Delta\xi_{rl} = (-1)^l \frac{\Delta\delta_r}{2n^{1/2}}\left[n - \frac{1}{1 - \cos\alpha}\right].$$

The second term in the brackets represents probably the error due to the fact that we have been using inexact values for the coefficients c_{kl}. It would have an important influence only in the case of very small values of α corresponding to very long waves.[14]

Dropping it we get finally

$$\Delta\xi_{rl} = (-1)^l \frac{1}{2}\Delta\delta_r n^{1/2} = (-1)^l \frac{1}{2}\frac{\Delta L_r}{n^{1/2}} \tag{18}$$

where $\Delta L_r = n\Delta\delta_r$ denotes the change of length of the whole bar in the r excited state. Since this change is actually due to the presence of one single excited atom, it must be practically independent of the total number of atoms, whence it follows that $\Delta\delta_r$ must be inversely proportional to n, a result which we have derived above from somewhat different considerations for the case of the real three-dimensional crystal. The preceding formula which we can safely extend to this case[15] thus means that the change of the normal coordinates, produced by the excitation of one atom out of n is inversely proportional to the *square root* of n. The coefficient of proportionality $\frac{1}{2}\Delta\delta_r n$ is determined by (15a) and can be shown to be of the order of magnitude of atomic dimensions.

Having established the relation between the normal coordinates of the nonexcited and those of the excited crystal we must now turn to the consideration of the Schrödinger wave functions of the corresponding "heat oscillators." These functions will be denoted by $f_{s,N_s}{}^0(\xi_s)$ for the N_s quantum state of the s-th oscillator in the case of the unexcited crystal and by $f_{s,N_s}{}^r(\xi_{rs})$ in the case of a crystal in the r-th state of an excitation multiplet. The general form of the functions $f_N(\xi)$ is given by the formula

$$f_N(\xi) = \left[2^N N!(\pi\alpha)^{1/2}\right]^{-1/2} H_N(\alpha^{1/2}\xi)e^{-1/2\alpha\xi^2} = f_N{}^*(\xi) \tag{19}$$

where H_N is Hermite's polynomial of the N-th degree and α is a constant proportional to the natural frequency of the oscillator ν. If the coordinate ξ is normalized in such a way that the energy of the oscillator is represented by

$$\frac{m}{2}\left[\left(\frac{d\xi}{dt}\right)^2 + 4\pi^2\nu^2\xi^2\right]$$

[14] In this case we should have

$$1 - \cos\alpha \cong \tfrac{1}{2}\alpha^2 = (l + \tfrac{1}{2})^2\pi/2n^2$$

and

$$c_{kl} \cong (-1)^l \frac{\Delta\delta_r}{n^{1/2}} \frac{n^2}{\pi^2(l + \frac{1}{2})^2}$$

[15] Replacing l by the sum $l_1 + l_2 + l_3$.

then[16]

$$\alpha = 4\pi^2 m\nu/h. \tag{19a}$$

The absolute value of α does not play any role since we can always replace the coordinate ξ by $\eta = \alpha^{1/2}\xi$. If however we have to compare the behavior of the same oscillator for two different values of the frequency parameter $\nu = \nu_0$ and $\nu = \nu_r$ then we must take into account the relative value of α which gives us two different wave functions of the form

$$f_N{}^0(\xi_1) = f_N(\xi_1) \text{ and } f_N{}^{(r)}(\xi_r) = f_N\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2}\xi_{rs}\right]. \tag{20}$$

The function $f_N(\xi)$ can be defined here and in the sequel by formula (5) with $\alpha = 1$.

5. Determination of the Probability of the Individual Transitions of a Crystal from the Excited to the Normal State (or *vice versa*).

The stationary states of the crystal, including the vibratory motion of the atoms can be described to a first approximation by a wave function Ψ equal to the product of an electronic function $\chi(1, 2 \cdots n)$ specifying the inner states of the atoms and of the functions (20) for all the $3n$ oscillators. We thus get for the r-th excited substate

$$\Psi_r = \chi_r(1, 2, \cdots n) \prod_{s=1}^{3n} f_{N_{rs}}\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2}\xi_{rs}\right] \tag{21}$$

and for the normal state

$$\Psi_0 = \chi_0(1, 2, \cdots n) \prod f_{N_{0s}}(\xi_s) \tag{22}$$

with

$$\chi_0 = \psi_1(1)\psi_1(2) \cdots \psi_1(n) \tag{22a}$$

which is obviously the same approximation to the electronic function of a number of atoms in the same state, as the functions χ_r defined by (8), are for the case when one of them is excited.

It must be remarked that whereas the factorization of the oscillator functions corresponds to the assumed absence of any direct coupling between them, the multiplication of these functions with the electronic function χ does not mean that there is no coupling between the vibratory and inner motion of the atoms, this coupling being in fact expressed (in an approximate manner of course) by the dependence of the vibration frequencies ν_{rs} upon the electronic state. Through this interaction of the electronic (inner) and the vibratory (outer) motion the different oscillators are actually coupled with each other—in a rather indirect way—and it is just this indirect coupling that enables the simultaneous transition of any number of oscillators

[16] Cf. A. Sommerfeld, Wellenmechanisches Ergänzungsband, p. 18. This normalization corresponds to the condition $\Sigma\xi_s^2 = \Sigma(\Delta\chi)_s^2$ or $\Sigma_l c_{kl}^2 = 1$ used above.

from one state, specified by the quantum numbers N_{01}, $N_{02} \cdots N_{03n}$ to another N_{r1}, $N_{r2} \cdots N_{r3n}$, if this transition is combined with an electronic one, that is with a transition of the crystal from the normal state to an excited one or *vice versa*.

The probability of such a combined transition is determined by the matrix element of the perturbation energy with respect to the functions (21) and (21a). This perturbation energy seems at first sight to be identical with the mutual potential energy of all the atoms U, which has been considered above in connection with its influence on the electronic motion. It will be remembered however, that this influence has been examined on the assumption that the atoms were at rest at the lattice points of the crystal, which corresponds to definite equilibrium values $R_{\alpha\beta}{}^0$ of the interatomic distances $R_{\alpha\beta}$ entering as parameters in the expression (3) for U.

Since we are now concerned with transitions due to the interaction of the electronic and vibratory motion it is necessary to take account of the change of the $R_{\alpha\beta}$'s and consequently of U which are due to the displacements of the atom from their equilibrium positions. This could be done by expanding U in a power series with respect to the differences $R_{\alpha\beta}-R_{\alpha\beta}{}^0$ and expressing the latter through the normal coordinates $\xi_1, \xi_2 \cdots \xi_{3n}$.

The series so obtained would contain next to the equilibrium value of U a sum of squares of the coordinates ξ which must be dropped out, since it represents nothing else but the potential energy of the oscillators (accounted for separately) and further higher powers of the ξ's which should represent a certain degree of anharmonicity and of direct coupling between the oscillators and at the same time a certain alteration of the electronic states as a result of the vibrational motion.

If we did not take into account the indirect coupling (and anharmonicity) expressed by the dependence of the vibration frequencies on the excitation state, we should have to carry out the expansion of U up to terms of the 100-th (or even higher) degree in the ξ's in order to get a nonvanishing probability for transitions involving a 100-fold jump of the oscillators (cf. Introduction). As a matter of fact, however, this is not necessary and we can safely stop at terms of the third order (as is done in the theory of the thermal expansion and thermal conductivity of solids) thus putting

$$U = U^0 + U''' \tag{23}$$

where

$$U''' = \sum_{k,l,m} A_{klm}\xi_k\xi_l\xi_m \tag{23a}$$

the coefficients A_{klm} being certain functions of the electronic (inner) coordinates $1, 2, \cdots n$.

The probability of radiationless transitions from the r-th excited state to the normal one (or *vice versa*) is determined by the matrix element of U with respect to the wave functions (21) and (22)

$$M_r \equiv \int U\psi_0^*\psi_r = \int \cdots \int \cdots \int U\chi_0^*\chi_r d\tau_1 \cdots d\tau_n \cdot \prod_{s=1}^{3n} f_{N_{0s}}(\xi_s) f_{N_{rs}}\left[\left(\frac{\nu_{rs}}{\nu_{0s}}\right)^{1/2}\xi_s\right] d\xi_s.$$

Of course only such states have to be considered which have the same or nearly the same energy (the corresponding transitions are usually denoted as "resonance" ones). The energy of the crystal in the normal state is equal to the sum of the energies of the separate atoms nW_I plus the equilibrium value of their mutual potential energy

$$\begin{aligned} W_0' &= \int \cdots \int U(\chi_0)^2 d\tau_1 \cdots d\tau_n \\ &= \sum_{\alpha<\beta} \iint V(\alpha, \beta; R_{\alpha\beta}) \left|\psi_1(\alpha)\right|^2 \left|\psi_1(\beta)\right|^2 d\tau_\alpha d\tau_\beta \end{aligned} \tag{25}$$

plus the vibrational energy

$$E_0 = \sum_{s=1}^{3n} h\nu_{0s}(N_{0s} + \tfrac{1}{2}). \tag{25a}$$

The energy of the same crystal in the excited state r is represented similarly by the sum

$$W_{II} + (n-1)W_I + W_r' + E_r$$

where W_r' is given by (8) and

$$E_r = \sum_{s=1}^{3n} h\nu_{rs}(N_{rs} + \tfrac{1}{2}). \tag{25b}$$

The condition for the radiationless transition to be a resonance one is thus expressed by the equation

$$W_{II} - W_I + W_r' - W_0' + \sum_{s=1}^{3n} [h\nu_{rs}(N_{rs} + \tfrac{1}{2}) - h\nu_{0s}(N_{0s} + \tfrac{1}{2})] = 0. \tag{26}$$

This equation can be approximately satisfied for a given r in a number of different ways corresponding to different jumps of the vibrational quantum numbers n_s. The total probability for the crystal to pass from the excited state into the normal one will be proportional to the sum of the squares of the matrix elements (24) (or rather their moduli) for all such "nearly resonance" transitions (see next paragraph).

In computing the matrix elements (24) we must express the normal coordinates of the excited crystal through those of the unexcited one by means of the relation (18). It is however to be kept in mind that these relations hold for the case when the ξ_s's are so normalized that $\Sigma_s \xi_s^2 = \Sigma \Delta x_s^2$, which corresponds to the value (19a) of the parameter α in the functions (19). If we put

$\alpha=1$ in (19), that is replace ξ_s by $\alpha^{1/2}\xi_s$ then in using the relations (18) we must multiply the right hand side by $\alpha^{1/2}$. Putting further $\nu_r/\nu_0=1+\Delta\nu_r/\nu_0$ and noticing that $\Delta\nu_r/\nu_0$ is a small quantity of the order of $1/n$ we can expand $f_N[(\nu_r/\nu_0)^{1/2}\xi_{rs}]=f_N[(\nu_r/\nu_0)^{1/2}(\xi_s+\Delta\xi_{rs})]$ in a series of powers of $1/n^{1/2}$

$$f_N[(\nu_r/\nu_0)^{1/2}\xi_{rs}] = f_N(\xi_s) + \Delta\xi_{rs}f_N'(\xi_s) + O(1/n) \tag{27}$$

$O(1/n)$ denoting the sum of terms of the order of magnitude $1/n$, $1/n^{3/2}$, etc. We shall presently see that all these terms can be dropped, their contribution to the total value of the transition probability (for all the possible individual transitions) decreasing with increase of n (as $1/n$ at least), whereas the contribution of the terms proportional to $\Delta\xi_{rs}$ that is to $1/n^{1/2}$ turns out to be independent of n (see below).

The change of the vibration frequencies connected with the excitation of the crystal is thus immaterial for the transitions we are considering, these transitions being due practically solely to the minute change of the equilibrium distance between the atoms.[17]

We shall first consider that part of M_r which corresponds to U^0 that is

$$M_r^0 = \int\cdots\int U^0\chi_0^*\chi_r d\tau_1\cdots d\tau_n \prod_{i=1}^{3n}\int f_{N_{0s}}(\xi_s)f_{N_{rs}}[(\nu_{rs}/\nu_{0s})^{1/2}\xi_{rs}]d\xi_s. \tag{28}$$

The contribution of each oscillator to M_r^0 is given according to (27) by the factor

$$I_r = \int f_{N_0}(\xi)f_{N_r}(\xi)d\xi + \Delta\xi_r\int f_{N_0}(\xi)f_{N_r}'(\xi)d\xi + O(1/n). \tag{29}$$

If $N_r=N_0$, this factor reduces practically to 1. If $N_r=N_0\pm1$ the first term on the right side vanishes but the second is different from zero, so that $I_r=O(1/n^{1/2})$. If $|N_r-N_0|>1$ the second term vanishes too and I_r turns out to be of the order of $1/n$ or still smaller.

We thus see that *only such transitions have to be taken into account, for which each oscillator either remains in the same state or jumps to the next one.*

From the well-known relation for Hermitian polynomials

$$\frac{d}{d\xi}H_N(\xi) = 2NH_{N-1}(\xi)$$

it follows, according to (19) (with $\alpha=1$):

$$f_N'(\xi) = (2^N N!\pi^{1/2})^{-1/2}2NH_{N-1}(\xi)e^{-\xi^2/2} - \xi f_N(\xi) = (2N)^{1/2}f_{N-1}(\xi) - \xi f_N(\xi)$$

whence for $N_r=N_0\pm1$

$$I_r = -\Delta\xi_r\int f_{N_0}(\xi)f_{N_r}(\xi)\xi d\xi = -\Delta\xi_r\xi_{N_r,N_0}$$

[17] This result applies to some extent to the case of diatomic molecules, where however the frequency shift also plays a marked rôle.

ξ_{N_r,N_0} being the matrix element of ξ. This matrix element is equal to $(N/2)^{1/2}$ where N is the larger of the two numbers N_r and N_0. We thus get for the s-th oscillator ($\Delta\xi_r$ being independent of s)

$$I_{rs} = -\Delta\xi_r(N_s/2)^{1/2} \quad (N_s = N_{0s}, N_{rs} \text{ if } N_{0s} = N_{rs} = \pm 1). \tag{29a}$$

(The same result can be derived directly from the well-known formula for the matrix element of the momentum, that is of the operator $(h/2\pi i)\,\partial/\partial\xi$). Hence it follows that in case of a transition in which p of the $3n$ oscillators jump simultaneously (to one of the next states), while the rest remain in the same state,

$$M_r^0 = \left[-\Delta\xi_r(N/2)^{1/2}\right]^p U_r^0 \tag{30}$$

where N is the geometrical mean of the p numbers N_s and

$$U_r^0 = \int \cdots \int U^0 \chi_0 \chi_r d\tau_1 \cdots d\tau_n.$$

We shall now briefly examine the second part of M_r, corresponding to U'''' (23a)

$$M_r''' = \sum_{klm} \int \cdots \int A_{klm}\chi_r\chi_0^* d\tau_1 \cdots d\tau_n \phi^r{}_{klm} \Pi'_{klm} \tag{31}$$

where $\phi^r{}_{klm}$ denotes the integral with respect to the coordinates ξ_k, ξ_l, ξ_m containing their product as a factor. This integral is a product of three simple ones with respect to the separate coordinates if the latter are all different, or of two simple ones if $k=l\neq m$; if $k=l=m$, it reduces to an integral with respect to one variable ξ_k containing its cube as a factor. Π'_{klm} denotes the product of factors (29) for all the other normal coordinates ξ. ϕ_{klm} is different from zero in that case only if the corresponding oscillators make together three elementary jumps ($|N_{rk}+N_{rl}+N_{rm}-N_{0k}-N_{0l}-N_{rm}|=3$), one jump each if they are all different, or a double jump and a simple one if $k=l\neq m$, or a single triple-jump if $k=l=m$.

If the total number of jumps performed by all the oscillators in the transition considered is to be equal to p, then in the product Π'_{klm} only $p-3$ factors of the type (29a) must appear, so that M_r''' may be written in the form

$$M_r''' = \sum_{klm} A^r_{klm}\phi^r_{klm}\left[-\Delta\xi_r(N/2)^{1/2}\right]^{p-3} \tag{31a}$$

$A^r{}_{klm}$ being the matrix element of A_{klm} $(1, 2, \cdots n)$ with respect to χ_0 and χ_r. One can say that in the product $\phi^r{}_{klm}\,\Pi'_{klm}$ the first factor refers to jumps which are due to the direct coupling between three or two oscillators (or their anharmonicity) and the second one to the indirect coupling provided by the dependence of the vibrations on the excitation state.

The coefficients A_{klm} can be obviously defined by the formula

$$A_{klm} = \sum_{\alpha\beta\alpha}\left(\frac{\partial^3 U}{\partial x_\alpha \partial x_\beta \partial x_\gamma}\right)_0 \frac{\partial x_\alpha}{\partial \xi_k}\frac{\partial x_\beta}{\partial \xi_m}\frac{\partial x_\gamma}{\partial \xi_n}$$

where $x_\alpha, x_\beta, x_\gamma$ denote the x, y, z coordinates of the atoms ($\alpha, \beta, \gamma = 1, 2 \cdots 3n$), and the differential coefficients $\partial x_\alpha / \partial \xi_k$, etc., are the transformation coefficients which in the unidimensional case considered above were denoted by c_{kl}, equation (17). Since these coefficients are of the order of magnitude of $1/n^{1/2}$, we see that M_r''', so far as its dependence upon n is concerned, is of the order of magnitude $(1/n^{1/2})^3 (1/n^{1/2})^{p-3} = (1/n^{1/2})^p$, that is, of the same order of magnitude as M_r^0 given by (30).

Now M_r^0 contains as factor the matrix element U_r^0 of the mutual potential energy of all the atoms in their normal equilibrium positions with respect to the functions χ_0 and χ_r, and this factor can be easily shown practically to vanish for all excited substates r with the exception of the one $r_1 = r_2 = r_3 = 0$ for which χ_r is symmetrical with respect to the inner coordinates $1, 2 \cdots n$ of all the atoms, that is representing an excitation wave of infinite length (having the same phase throughout the whole crystal). In fact using the expressions (8) for $\chi_r = \chi_{r_1 r_2 r_3}$ and (22a) for $\chi_0 = \phi_0$, we have

$$U_r^0 = \sum_{k_1 k_2 k_3} c_{rk} \int \cdots \int U^0 \phi_0^* \phi_k d\tau_1 \cdots d\tau_n$$

where $\phi_0 = \psi_I(1)\psi_I(2) \cdots \psi_I(n)$, and ϕ_k is obtained from ϕ_0 by replacing the factor $\psi_I(k)$ by $\psi_{II}(k)$. Introducing here the expression (3) for $U = U^0$ we get $\int \cdots \int U^0 \phi_0^* \phi_k d\tau_1 \cdots d\tau_n$ = sum of integrals of the type

$$\iint U(k, l; R_{kl}) \psi_I^*(k) \psi_{II}(k) \psi_I^*(l) \psi_I(l) d\tau_k d\tau_l$$

with respect to all values of l. Now this sum must obviously be practically independent of k, that is of the location of the atom k within the crystal—so far as *surface effects can be neglected*. Thus the preceding expression for U_r^0 reduces to the product of a constant by the sum $\Sigma_k c_{rk}$ which vanishes (practically, again neglecting surface effects) unless $r_1 = r_2 = r_3 = 0$.

It seems questionable whether the excited substate $r_1 = r_2 = r_3 = 0$ has actually to be taken into account or not. But even if we do not exclude it, we see that the probability of a transition from this state to the normal one, so far as it is determined by U_r^0 need not be much larger than that determined by U_r''' for similar transitions from all the other excited substates, that is transitions involving the same number p of heat oscillators or rather of elementary jumps. The matrix component M_r for such transitions having the order of magnitude $(1/n^{1/2})^p$ the corresponding probability will be proportional to $(1/n)^p$. The coefficient of proportionality cannot be determined accurately unless we restrict ourselves to transitions from the substate $r_1 = r_2 = r_3 = 0$ and neglect U''' with respect to U^0. In this rather fictitious case (which it will however be well to consider for the sake of illustrating that part of the theory which is connected with the dependence of the resulting total probability upon the number of atoms n), the probability of a transition involving the cooperation of p heat oscillators, or rather *the square of the corresponding matrix element*, is given, according to (30) and (18), by

$$M_r^2 = \left| U_r^0 \right|^2 \mu_r^p \tag{32}$$

where

$$\mu_r = \frac{\alpha(\Delta L_r)^2}{8} \frac{N}{n} \tag{32a}$$

L_r being an abbreviation for the product $\Delta\delta_r n$, and α being defined by (19a). α is the reciprocal of the square of a distance which depends upon the frequency ν_s of the corresponding oscillator. For oscillators of the maximum frequency in the acoustical spectrum $\nu_0 \cong 10^{13}$ this distance $1/\alpha^{1/2}$ is equal to $3\times 10^{-9}/m_H^{1/2}$ cm where m_H is the atomic weight of the crystalline element we are considering with respect to hydrogen. We thus see that the product $\alpha(\Delta L_r)^2$ must be of the order of magnitude 1, at least for the higher frequency oscillators. For oscillators of lower frequencies it must however be smaller, so that these oscillators must be less effective in the transformation of the excitation energy into heat energy not only because their share is smaller, but because they have a smaller probability of getting this share.

In (32a) α and N denote certain (geometrical) mean values for all the p oscillators participating in the transition. Denoting the value of α for oscillators of the highest frequency with α_0, we can put

$$\mu_r = \frac{\alpha_0(\Delta L_r)^2}{8n}\left(\prod_p \frac{\nu_s}{\nu_0} N_s\right)^{1/p} \tag{32b}$$

where $\prod_p$ denotes the product over all the p oscillators we are considering.

6. The Resulting (Statistical) Value of the Probability of Radiationless Transitions

The minimum value of $p = p_0$ is obtained if only oscillators of the highest frequency or next to it are taken into account. This minimum value is given by

$$p_0 = \frac{E_0 - E_r}{h\nu_0} = \frac{W_{II} - W_I + W_r' - W_0'}{h\nu_0} \tag{33}$$

according to (26), and as was mentioned above is of the order of magnitude of 100. Now these oscillators can be picked up from a much larger number Q of oscillators whose frequencies are enclosed within an interval $\nu_0 - \nu = D\nu$ which can be extremely small with respect to ν but at the same time large enough to make Q exceedingly large compared with p. Limiting ourselves to longitudinal waves (which for the same wave-length possess a higher frequency than the transverse ones), we have

$$Q = \frac{4\pi v}{u^3}\nu_0^2 D\nu$$

where v is the volume of the crystal and u the velocity of the longtitudinal waves, or since $v = n\delta^3$ and $(u/\nu_0)^3 = \lambda_0^3 = 4\pi\delta^3/3$

$$Q = 3nD\nu/\nu_0. \tag{33a}$$

It must be emphasized that for a given value of $D\nu$ (or $D\nu/\nu_0$) Q *is proportional to the total number of atoms forming the crystal.* Taking $n \geqq 10^{21}$ (which corresponds to a crystal with a volume about 1 cm³) and $D\nu/\nu_0 = 10^{-13}$, say, we get $Q = 3 \times 10^8$ which is still a million times larger than p_0.

Our p_0 oscillators can be picked up from the set containing Q of them *in a number of different ways*, this number being equal to

$$\binom{Q}{p_0} = \frac{Q(Q-1)\cdots(Q-p_0+1)}{1\cdot 2\cdots p_0} \geqq \frac{Q^{p_0}}{p_0!}$$

that is according to (33a) proportional to the p_0-th power of the total number of atoms n.

The total probability of a transition of the crystal from the excited state to the normal one, in which the excitation energy will be shared by *any* p_0 of the Q high frequency oscillators will thus be proportional to the product

$$M_r^2\binom{Q}{p_0} = |U_r^0|^2 \frac{(\mu_r Q)^{p_0}}{p_0!} = \frac{|U_r^0|^2}{p_0!}\left(\frac{3}{8}\alpha(\Delta L_r)^2 N \frac{D\nu}{\nu_0}\right)^{p_0} \tag{34}$$

that is, will be *independent of* n.

The fact that it turns out to be dependent upon the choice of the interval $D\nu$ is naturally explained by our having restricted ourselves to this interval. We can obtain some approximation to the value of the probability of any transition from the excited state to the normal one, or rather to the total value of ΣM_r^2 determining this probability by taking, in the above formula $D\nu/\nu_0 \geqq 1/2$ and replacing p_0 by a somewhat larger number $p = 2p_0$ say.

The problem of the determination of the resulting transition probability P_r can be solved exactly by a method which we are presently going to describe. It must be remarked however that in deriving this probability we must not restrict ourselves to the consideration of such transitions only, for which *all* the participating oscillators jump to a higher level. On the contrary we must take account of such transitions (which are under some circumstances by far the more frequent) in which some of the oscillators jump to a higher level and others to the lower one, adding, so to say, their energy to the excitation energy.

Further it must be remembered that the "resonance condition" expressed by the equation (26) or

$$E_0 - E_r = W_{II} - W_I + W_r' - W_0'$$

need not be *exactly* satisfied. In fact we have to consider, theoretically, transitions for which the difference $E_0 - E_r$ has any value whatsoever. Let us denote the sum ΣM_r^2 for all transitions for which the value of $E_0 - E_r$ is enclosed between E and $E+dE$ by $S(E)dE$. Then the transition probability which is actually observed referred to unit time is given by [18]

$$P_r = \frac{4\pi^2}{h} S(E) \tag{35}$$

[18] See, for instance, J. Frenkel, Einführung in die Wellenmechanik p. 211, formula (72a).

E being the resonance value of E_0-E_r, that is, the excitation energy of the crystal, defined by the right hand side of equation (26). E_0-E_r can be expressed as the sum $\Sigma p_s\epsilon_s$ over all the $3n$ oscillators, where $\epsilon_s=h\nu_s$ are the corresponding energy quanta and $p_s=0$, $+1$, or -1 for an oscillator not partaking in the transition, jumping to the next higher level, and the next lower level respectively. The total number of oscillators participating in the transition p is thus equal to $\Sigma|p_s|$, and the excess of oscillators gaining energy over those loosing it Σp_s. It must be remarked that for low temperatures, and in the case of the high frequency oscillators even for room temperatures jumps of the second kind (down) may not be possible, the corresponding oscillators being in the lowest state ($N_{rs}=0$)

We shall first neglect these downward transitions, that is, restrict ourselves to the non-negative values of p_s (0, 1). We shall further, for the sake of simplicity, take the same value of μ_r given by (32a) for all the oscillators (see below).

Our problem then reduces to the determination of the value of the sum

$$\sum{}'\mu_r{}^p = S(\epsilon)d\epsilon/|U_r{}^0|^2$$

for all values of the $p_s(=0, 1)$ satisfying the condition

$$E \leqq \sum p_s\epsilon_s \leqq E + dE \tag{36}$$

p being equal to the sum Σp_i. This problem is quite similar to the familiar problem met with in the Pauli-Fermi statistics of a gas with a given total energy E the p_s representing the possible numbers of particles in the s-th state. From the physical point of view they differ by the fact that instead of calculating the *number of states* of the whole system, that is the sum $\Sigma 1$ under the restriction (36) (the logarithm of $\Sigma 1$ being defined as the entropy), we have to calculate the sum $\Sigma\mu_r{}^p$, and further by the fact that E does not actually represent the energy of the system of oscillators but the change of this energy, the *states* thus being replaced by the *transitions*.

The restriction (36) can be removed by considering instead of the sum $\Sigma'\mu_r{}^p$ the sum $\Sigma\mu_r{}^pe^{-\beta E}$ with suitably adjusted parameter β (corresponding to the reciprocal of the temperature), extended over all possible values of the p_s. The second (unrestricted) sum is of course different from the first (restricted) one, but there exists a simple approximate relation between them. Writing the unrestricted sum in the form

$$\sum\mu_r{}^pe^{-\beta E} = \int_0^\infty S(E)e^{-\beta E}dE$$

(the factor $1/|U_r{}^0|^2$ is dropped for the sake of brevity), we see that the integrand $S(E)e^{-\beta E}$ must have a maximum for some value of E, which by a suitable choice of $\beta(>0)$ can be made to coincide with the given value E_m lying in the interval (36). If this maximum is sharp enough, which is actually the case when E_m is not too small, we can replace the function $S(E)e^{-\beta E}$ by a Gaussian function

$$S(E_m)e^{-\beta E_m}e^{-(E-E_m)^2/\gamma^2}$$

where the parameter γ measures the width (or sharpness) of the maximum.

This gives

$$\sum \mu_r{}^p e^{-\beta E} = S(E_m)e^{-\beta E_m}\int_{-\infty}^{+\infty} e^{-(E-E_m)^2/\gamma^2}d(E-E_m) = S(E_m)e^{-\beta E_m}\gamma\pi^{1/2}$$

or

$$S(E_m) = \frac{e^{\beta E_m}}{\gamma\pi^{1/2}}\sum \mu_r{}^p e^{-\beta E} \tag{37}$$

where the (unrestricted) summation on the right hand side has to be carried out exactly.

The specified value of the parameter β can be easily determined from the condition that the "average" value E for the curve $S(E)e^{-\beta E}$ practically coincides with the extremal value E_m. This gives

$$\overline{E} = \frac{\int ES(E)e^{-\beta E}dE}{\int S(E)e^{-\beta E}dE} = -\frac{\partial}{\partial\beta}\log\int S(E)e^{-\beta}\,dE = E_m$$

or

$$E_m = -\,\partial \log Z/\partial\beta \tag{37a}$$

where

$$Z = \sum \mu_r{}^p e^{-\beta E} \tag{37b}$$

is the analogue of the "state-sum" (Zustandssumme) of the usual statistical theory. The determination of the parameter γ requires some approximate knowledge of the function $S(E)$ and can be effected after the evaluation of $S(E_m)$ according to (37).

We have

$$Z = \sum_{p_1,p_2\cdots} \mu^{(p_1+p_2+\cdots)}e^{-\beta(p_1\epsilon_1+p_2\epsilon_2+\cdots)} = \prod_s \sum_{p^s}\mu_r{}^{p_s}e^{-\beta p_s\epsilon_s}$$
$$= \prod_s(1+\mu_r e^{-\beta\epsilon_s})$$

whence

$$\log Z = \sum_s \log(1+\mu_r e^{-\beta\epsilon_s}) = \int_0^{\epsilon_0}\log(1+\mu_r e^{-\beta\epsilon})g(\epsilon)d\epsilon \tag{38}$$

$g(\epsilon)d\epsilon$ being the number of oscillators whose energy quanta $\epsilon = h\nu$ lie between ϵ and $\epsilon+d\epsilon$. Restricting ourselves to longitudinal waves we have

$$g(\epsilon)d\epsilon = 3n\epsilon^2 d\epsilon/\epsilon_0{}^3.$$

Now μ_r being a very small number (of the order of $1/n$) we can put with sufficient accuracy

$$\log (1 + \mu_r e^{-\beta\epsilon}) = \mu_r e^{-\beta\epsilon}$$

which gives

$$\log Z = \frac{3n\mu_r}{\epsilon_0^3} \int_0^{\epsilon_0} e^{-\beta\epsilon} \epsilon^2 d\epsilon. \tag{38a}$$

This formula shows at once that Z *is actually independent of* n; the same follows from (37) and (37a) for β and for $S(E_m)$, the quantity which determines the probability for which we are looking.

The above results can be easily generalized to allow for the difference of the factor μ_r for different oscillators. Replacing μ_r^p by the product $\Pi\mu_{rs}^{p_s}$ we get formulae of the same type as before. In evaluating $\log Z$ according to (38) or (38a) we have to consider μ_r as a function of the index s or of the energy $\epsilon(=\epsilon_s)$.

Denoting the value of μ_{rs} for $\epsilon = \epsilon_0$ and $N_s = 1$ with μ_r we have

$$\mu_{rs} = \mu_r \epsilon_s N_s / \epsilon_0$$

so that instead of (38a) we get

$$\log Z = \frac{3n\mu_r}{\epsilon_0^4} \int_0^{\epsilon_0} e^{-\beta\epsilon} \epsilon^3 N(\epsilon) d\epsilon. \tag{39}$$

The average value of $N(\epsilon)$ at the temperature T under the assumption of statistical equilibrium is given by Planck's law $N(\epsilon) = 1/(e^{\epsilon/kT} - 1)$. If we assume this distribution to hold for the initial (excited) state of the crystal then (since $N_{rs} = N_{0s} - 1$) the preceding expression has to be increased by 1, the average value of $N(\epsilon)$ thus being

$$N(\epsilon) = 1/(e^{\epsilon/kT} - 1) + 1 = 1/(1 - e^{-\epsilon/kT}). \tag{39a}$$

The above theory can be applied to the estimation of the probability of transitions of the opposite character, that is from the normal state to the excited one, so far as all the participating oscillators jump in the same sense, that is downwards, their energy being converted into the excitation energy. In this case we have to put of course

$$N(\epsilon) = 1/(e^{\epsilon/kT} - 1). \tag{39b}$$

It can be easily shown that our simplified theory, which takes into account jumps of the same sense only, holds for the limiting case that the product $n\mu_r$ (which is independent of n and which is a measure of the change of atomic distance produced by excitation) is very small. The probability of transitions in which p oscillators take part being approximately proportional to $(\mu n)^p/p!$ (cf. equation (34)) a strict economy in the use of the different oscillators will be observed in this case, their number being reduced to the minimum $p_0 = (E_0 - E_r)/h\nu_0 = E_m/\epsilon_0$ and "useless" jumps in the wrong sense practically excluded.

To get a rough idea of what will take place in the opposite case, that is if μn is large, we have to sum up the preceding expression for all values of p starting with $p=p_0$. If $\mu n \ll p_0$ this sum will still practically reduce to the first term. If however $\mu n \gg p_0$ it can be replaced by the sum $\sum_{p=1}^{\infty}(\mu n)^p/p!$ giving $e^{\mu n}$. The same result is obtained by replacing the sum by its maximum term, which corresponds to $p=\mu n$ and putting $p!=(p/e)^p$.

The method applied above for the approximate evaluation of the restricted sum of the products $\mu_{rs}|^{p_s}|$ is no longer applicable when the numbers p_s are allowed to take negative values (-1), for the simple reason that the function $S(E)$ has no tendency to increase in this case with increase of E. To the contrary it has a very flat maximum for $E=0$ and vanishes for $|E|>\Sigma\epsilon_s$. One could get rid of this restriction $E<\Sigma p_s\epsilon_s<E+dE$ in this case by a more general method, involving the use of Dirichlet's disruptive multiplier.[19] It does not seem worth while however to develop this method at a greater length here and we shall satisfy ourselves by making a direct calculation for the simplified case $\epsilon_s=\epsilon=\text{const}$. Our problem can then be stated as follows: The number n is expressed as the sum of three numbers $n'+n''+n'''$, denoting respectively the number of positive, negative and zero values in the sequence $p_1, p_2 \cdots p_n$; to determine the sum $\Sigma'\mu^{n'+n''}$ under the restriction that $n'-n''=p_0=E/\epsilon$.

Since each "partitio" $n=n'+n''+n'''$ can be effected in $n!/n'!n''!n'''!$ different ways (by permuting the numbers p_i) we get

$$\Sigma'\mu^{n'+n''}=\sum_{n''=0}^{n-p}\frac{n!}{n'!n''!n'''!}\mu^{n'+n''}(n'=n''+p_0,\ n'''=n-2n''-p_0).$$

The ratio of the n''-th term of this sum to the preceding one is equal to

$$(n-2n''+p_0+1)(n-2n''+p_0+2)\mu^2/n''(n''+p_0)$$

or approximately so long as n'' is small compared with n

$$(n\mu)^2/n''(n''+p_0).$$

The maximum term is that for which this ratio is equal to 1, the condition $n''\ll n$ being obviously satisfied for $n''(n''+p_0)=(n\mu)^2$. Replacing the sum by its maximum term we have

$$\Sigma'\mu^{n'+n''}\cong(n\mu)^{n'+n''}/n'!n''!$$

This gives if $n''\gg 1$ using Stirling's formula

$$\Sigma'\mu^{n'+n''}=\frac{(n\mu e)^{2n''+p_0-1}}{2\pi n''^{n''}(n''+p_0)^{n''+p_0}} \tag{40}$$

where

$$n''=[(n\mu)^2+(p_0/2)^2]^{1/2}-p_0/2. \tag{40a}$$

[19] That is the integral $\int_0^\infty sn\,ax\cos bx\,dx/x$ which is equal to $\pi/2$ for $a>b$, $-\pi/2$ for $a<b$ and $\pi/4$ for $a=b$.

If $n\mu$ is much larger than p_0 we can put $n''=n\mu$ and reduce the above sum to

$$\sum{}'\mu^{n'+n''} \leqq e^{2n\mu+p_0}/2\pi n\mu.$$

In the opposite case ($n\mu \ll p_0$) we have $n'' \leqq (n\mu)^2/p_0$, the result given by (40) being practically the same as in the case $n''=0$ which corresponds to one-sided jumps, that is

$$\sum{}'\mu^{n'+n''} \leqq (n\mu)^{p_0}/p_0!$$

Which case is usually met with in practice, is difficult to say.

7. Radiative Transitions (Absorption and Emission of Light)

We have considered heretofore only radiationless transitions of the crystal from the excited state to the normal one or vice versa. We must now briefly examine such transitions which are connected with the absorption or emission of light. As has been pointed out in the introduction the excitation of a crystal by incident radiation forms the first stage of the process of light absorption, the second stage being provided by the radiationless transition to the normal state.

The energy levels or spectral terms which have to be considered in this connection are those that have been discussed already in the preceding sections, the energy of one of the excited sub states with respect to the normal state being given by (26). Since there are n-substates, corresponding to one single excitation state of an isolated atom, there must appear in the spectrum of a solid body in general n lines, corresponding to one single line in the spectrum of the gas, so far of course as the initial or the final state is the normal one. The frequencies of these lines, which can be described as forming an "excitation multiplet" are given by

$$\nu_r = (1/h)(W_{II} - W_I - W_0') + W_r'/h \tag{41}$$

if vibrational transitions are not taken into account. Allowing for these transitions we get a still larger number of spectral lines with frequencies differing from the preceding ones by the amounts

$$\Delta\nu_r = \sum[\nu_{rs}(N_{rs}+\tfrac{1}{2}) - \nu_{0s}(N_{0s}+\tfrac{1}{2})]. \tag{41a}$$

The spacing between the main lines (41) is determined approximately by the expression (15) or (8a). It is the smaller, the larger the number of atoms in the crystal. The total width of the multiplet formed by all these lines, is however independent of n and equal approximately to V_0+6V_1, where

$$V_0 = \int\int U(k,l)\,|\,\psi_{II}(k)\,|^2\,|\,\psi_I(l)\,|^2 d\tau_k d\tau_l \tag{42}$$

and (for the case of a simple cubical lattice)

$$V_1 = 6\int\int U(k,l)\psi_{II}^*(k)\psi_I(k)\psi_I^*(l)\psi_{II}(l)d\tau_k d\tau_l \tag{42a}$$

k and l denoting two neighboring atoms. This width is of the same order of magnitude, or perhaps just a few times larger, than the shift in the spectral levels of two atoms, produced by their combining together into one molecule. The maximum spacing between the lines of such a multiplet is of the order of $2V_1/n$, that is, so small that they should appear in practice as a continuous band even if they had no satellites due to the accompanying vibrational jumps and no natural width, which is measured by the probability of radiationless transitions we have examined before. This natural width (equal to the "mean life" of the corresponding excited substate), being independent of n must be much larger than the spacing between the consecutive lines. We thus see that the resolution of the continuous (band) spectrum of a solid body into single lines, which has been observed by J. Becguerel in the spectra of some rare earths at the temperature of liquid air and recently by W. Obreimow[20] in iodine and other substances at very low temperatures (of liquid hydrogen or helium) cannot be explained without special assumptions about the separation of the lines of an excitation multiplet or their intensities.

It can occur, namely, that for some excitation state II the "exchange energy" (42a) is abnormally small, so that the whole multiplet will appear as a single line, accompanied by satellites due to the vibration jumps. Since the coupling of the electronic states with the vibrational ones is determined partially by the same energy V_1, as the width of the excitation multiplet (see for instance formula (15a) for the change of the crystal lattice δ), these satellites will be rather faint. This may account for the lines observed by Becquerel, which were not very much influenced by the temperature.

Another possible explanation is that only a few of the excited sub-levels can combine with the normal one, these combinations forming a series of more or less widely spaced lines. Now the natural width of these lines due to radiationless transitions will be the smaller the lower the temperature, for as we have seen the coefficients μ_{rs} which determine the probability of such transitions are proportional to the average values of the quantum numbers N_s and must therefore decrease as the temperature decreases. At the same time and in the same measure will the intensity of the satellites decrease due to vibrational jumps. It can thus happen that for sufficiently low temperatures the continuous spectrum of the solid body will be resolved into separate lines, in accordance with Obreimow's observations.

It is however hardly possible to substantiate the above explanation by actual calculation of the intensities of spectral lines, that is of the probabilities of transitions connected with absorption or emission of radiation.

In the simple case of an atom or a molecule these probabilities are determined by the matrix elements of the resulting electric moment of the system. In the case of a molecule consisting of n identical atoms this sum is a symmetrical function of their electronic coordinates $1, 2, \cdots n$. Replacing the molecule by a crystal and considering pure electronic transitions not accompanied by vibrational jumps, we get for the matrix element of this

[20] W. Obreimow and Proc. Amsterdam Acad. de Kaas 31-3, p. 353 (1928).

symmetrical function $P(1, 2, \cdots n)$ with respect to the functions χ_r and χ_0 a value which can be shown to be zero for all the excited substates with the exception of the symmetrical one (by the same argument as in Section 5). It thus seems that, as a matter of fact, the whole multiplet will be reduced to one single line, or there will be no lines whatever if the symmetrical excitation state cannot be realized.

This argument is however fallacious, for in the case of a crystal whose linear dimensions are large or even comparable with the wave-length of the absorbed or emitted light the probability of absorption or emission will be determined not by the resultant electric moment $P(1, 2, \cdots n)$ but by a sum of the moments of the separate atoms $P_k(k)$ multiplied with *certain phase factors, which depend upon the positions of these atoms* R_k. In case of a system of plane electromagnetic waves (of resonance frequency) propagated within the crystals in the direction x, say, with the phase velocity w, these factors would be $e^{i2\pi\nu x k/w}$, so that the probability of absorption of a single light quantum, that is of the excitation of a single atom, would be measured by the matrix elements with respect to the functions χ_r and χ_0 of the sum $\Sigma P_0(k)e^{i2\pi\nu x k/w}$. There is no reason why these matrix elements should vanish for most of the substates r, remaining different from zero for a few others.

The computation of the excitation probabilities by the above method can hardly give perfectly correct results, a more consequent quantum-mechanical treatment being necessary in order to obtain them, but it seems fairly certain on the basis of these crude considerations, that nothing like a selection rule for the different terms of an excitation multiplet can be expected to exist.

It is possible that the phenomenon observed by Obreimow is limited to the case of compound substances, which lie outside the scope of this investigation. Preliminary results which I have obtained for such compound crystals, seem to support this conclusion.

BAND SPECTRUM INTENSITIES FOR SYMMETRICAL DIATOMIC MOLECULES. II

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Abstract

In a previous paper the writer derived an approximate expression for intensities in the electronic vibrational bands of symmetrical diatomic molecules, based upon the Franck-Condon theory of transition probabilities. In the present paper the approximation is carried further, by removing the restriction that the oscillations be linear. An extended formula is given making use of the Schrödinger theory of perturbations.

Calculations using this perturbation theory formula are carried out for the hydrogen absorption band spectrum. It is shown that the agreement with experiment is much improved over that obtained on the assumption of harmonic oscillations. Calculations are also made using Morse's potential function in which case the agreement is still further improved, especially for the higher transitions.

I. Introduction

IN A recent[1] paper the writer derived a formula expressing the intensities of the electronic-vibrational bands of symmetrical diatomic molecules as a function of the change in separation of the atoms and the change in the binding force between the atoms caused by the electronic transition. Since the present paper is essentially an extension of the results there obtained, the above paper will be referred to as Part I. The formula developed in Part I was used to calculate the intensities in the absorption spectra of several molecules and approximate agreement with experiment was obtained. Exact agreement was not to be expected due to the fact that the experimental temperatures were unknown and because of the approximations which had to be made in order to carry through the calculations. Three essential assumptions in deriving the intensity formula were: (1) that the complete wave function could be expressed as a product of a function of the electronic coordinates only and a function of the nuclear coordinates only; (2) that the electric moment could be separated into two parts, one of which was constant over the electron integration and the other constant over the nuclear integration and; (3) that the oscillations of the nuclei were simple harmonic. The last assumption was made not because of any theoretical necessity but merely to simplify the algebraic evaluation of the integrals involved. It is the purpose of this second part to extend the formula developed in Part I to the case in which the nuclear oscillations are nonharmonic.

II. Application of the Perturbation Theory

In order to take care of the deviation of the nuclear oscillations from simple harmonic motion, the potential energy between the nuclei may be

[1] E. Hutchisson, Phys. Rev. **36**, 410 (1930).

expressed as a power series in a factor depending upon the displacement of the nuclei from their equilibrium separation r_e*. The Schrödinger equation in this case is:

$$\nabla^2\Psi + 8\pi^2\mu/h^2[W - 2\pi^2\omega_e{}^2I_e\{\xi^2 + c_3\xi^3 + c_4\xi^4 + \cdots\}]\Psi \tag{1}$$

where Ψ = the Schrödinger wave function, W = total energy, μ = the equivalent mass, h = Planck's constant, $\xi = (r - r_e)/r_e$, I_e = moment of inertia at equilibrium separation and ω_e, c_3 and c_4 are constant coefficients in the potential energy. The radial part of the wave equation then has the following form[2]: (letting $\xi = [h^{1/2}/2\pi(\omega_e I_e)]\eta$)

$$\begin{aligned} F'' + [\{2W/h\omega_e - kK(K+1) - \eta^2\} + k^{1/2}\{2kK(K+1)\eta - c_3\eta^3\} \\ + k\{-3kK(K+1)\eta^2 - c_4\eta^4\}]F = 0 \end{aligned} \tag{2}$$

where $k = h/4\pi^2\omega_e I_e$ and K is the rotational quantum number.

The normalized solution of this equation in the first approximation, in which only the first term is considered since k usually has a value less than 0.01, is:

$$F_v{}^0 = (2^v v!\pi^{1/2})^{-1/2}e^{-\eta^2/2}H_v(\eta) \text{ and} \tag{3}$$

$$W_v{}^0 = h\omega_e(v + \tfrac{1}{2}) + (h^2/8\pi^2 I_e)K(K+1) \tag{4}$$

where v is the vibrational quantum number and H is the Hermitian polynominal.

The perturbation terms in the radial waves equation are therefore:

$$V_1 = (k^{1/2}h\omega_e/2)[2kK(K+1)\eta - c_3\eta^3] \tag{5}$$

$$V_2 = (kh\omega_e/2)[-3kK(K+1)\eta^2 - c_4\eta^4]. \tag{6}$$

According to Schrödinger's perturbation theory,[3] we have for the complete wave function:

$$F_v = F_v{}^0 + F_v{}^1 + F_v{}^2 + \cdots = F_v{}^0 + \sum_i A_{vi}F_i{}^0 + \sum_j B_{vj}F_j{}^0 + \cdots \tag{7}$$

where

$$A_{vi} = \int V_1F_v{}^0F_i{}^0d\eta \Big/ (W_v{}^0 - W_i{}^0) \tag{8}$$

and

$$\begin{aligned} B_{vj} = \frac{\int V_2F_v{}^0F_j{}^0d\eta}{W_v{}^0 - W_j{}^0} + \sum_{e=0}^{\infty}\frac{\int V_1F_v{}^0F_e{}^0d\eta \int V_1F_e{}^0F_j{}^0d\eta}{(W_v{}^0 - W_j{}^0)(W_v{}^0 - W_e{}^0)} \\ - \int V_1F_v{}^0F_j{}^0d\eta \int V_1F_v{}^0F_v{}^0d\eta \Big/ (W_v{}^0 - W_j{}^0)^2 \end{aligned} \tag{9}$$

* r_e is used in this part in place of the r_0 of Part I in order that the notation conform with that recommended by band spectroscopists, c.f., R. S. Mullikan, Phys. Rev. **36**, 611 (1930.)

[2] E. Fues, Ann. d. Physik **80**, 367 (1926).

[3] E. U. Condon and P. M. Morse, Quantum Mechanics, pp. 118 ff.

where $v \neq i$ and $v \neq j$ and the limits of integration are taken from $\eta = -\infty$ to $+\infty$ instead of from -1 to $+\infty$ since the addition of the region from -1 to $-\infty$ will not appreciably affect the value of the integral for small quantum numbers. Also we have:

$$A_{vv} = 0 \text{ and } B_{vv} = -\tfrac{1}{2}\sum_i (A_{vi})^2. \tag{10}$$

To evaluate the integrals in the perturbation terms we make use of the recursion formulas

$$\begin{aligned}
\eta F_v^0 &= [(v+1)/2]^{1/2} F_{v+1}^0 + [v/2]^{1/2} F_{v-1}^0 \\
\eta^2 F_v^0 &= [(v+1)(v+2)/2^2]^{1/2} F_{v+2}^0 + [(2v+1)/2] F_v^0 + [v(v-1)/2^2]^{1/2} F_{v-2}^0 \\
\eta^3 F_v^0 &= [(v+1)(v+2)(v+3)/2^3]^{1/2} F_{v+3}^0 + [3^2(v+1)^3/2^3]^{1/2} F_{v+1}^0 \\
&\quad + [3^2 v^3/2^3]^{1/2} F_{v-1}^0 + [v(v-1)(v-2)/2^3]^{1/2} F_{v-3}^0 \\
\eta^4 F_v^0 &= [(v+1)(v+2)(v+3)(v+4)/2^4]^{1/2} F_{v+4}^0 \\
&\quad + [(v+1)(v+2)]^{1/2}[(2v+3)/2] F_{v+2}^0 + 3[(v+1)^2 + v^2]/2^2 F_v^0 \\
&\quad + [v(v-1)]^{1/2}[(2v-1)/2] F_{v-2}^0 + [(v-3)(v-2)(v-1)v/2^4]^{1/2} F_{v-4}^0.
\end{aligned}$$

The values obtained from these recursion formulas are now substituted in the integrals occurring in (8) and (9). The terms in V_1 and V_2 which depend upon the rotational quantum numbers may be neglected if we apply our results to only transitions between the first few rotational quantum states, since for actual molecules k is much smaller than c_3 or c_4. We then obtain the following values for the constants:

$$\begin{aligned}
B_{v,v+4} &= C_{v,v+4} = (1/128)[kc^2{}_3(4v+7) + 4kc_4][(v+1)(v+2)(v+3)(v+4)]^{1/2} \\
A_{v,v+3} &= C_{v,v+3} = (k^{1/2}c_3/12\cdot 2^{1/2})[(v+1)(v+2)(v+3)]^{1/2} \\
B_{v,v+2} &= C_{v,v+2} = (1/64)[kc_3{}^2(7v^2+33v+27) + 8kc_4(2v+3)][(v+1)(v+2)]^{1/2} \\
A_{v,v+1} &= C_{v,v+1} = (9k^{1/2}c_3/12\cdot 2^{1/2})[v+1]^{3/2} \\
B_{v,v} &= C_{v,v} = -(kc_3{}^2/576)[164v^3 + 246v^2 + 256v + 87] \\
A_{v,v-1} &= C_{v,v-1} = -(9k^{1/2}c_3/12\cdot 2^{1/2})[v]^{3/2} \\
B_{v,v-2} &= C_{v,v-2} = (1/64)[kc_3{}^2(7v^2 - 19v + 1) - 8(2v-1)][v(v-1)]^{1/2} \\
A_{v,v-3} &= C_{v,v-3} = -(k^{1/2}c_3/12\cdot 2^{1/2})[v(v-1)(v-2)]^{1/2} \\
B_{v,v-4} &= C_{v,v-4} = (1/128)[kc_3{}^2(4v-3) - 4kc_4][v(v-1)(v-2)(v-3)]^{1/2}.
\end{aligned}$$

Since all the A's and B's except those given above are equal to zero we may write the complete wave function in the simple form

$$F_v = \sum_{j=v-4}^{v+4} C_{vj} F_j^0. \tag{11}$$

To obtain a complete expression for the intensity amplitudes it is only necessary to substitute our new wave function into the final expression

(Eq. 11)[4] of Part I. It is hardly worth while to make the substitution explicitly since the resulting expression would take up too much space and would be too cumbersome to use efficiently. However if we have a set of values calculated from the formula of Part I we may immediately obtain the corrected intensity amplitudes from:

$$I_{v'v''} = \sum_{k=v'-4}^{v'+4} \sum_{j=v''-4}^{v''+4} C_{v'k} C_{v''j} I_{kj}^{0}. \tag{12}$$

This expression contains in general 81 terms and therefore requires long calculations to get the required corrected intensities. The expression may be greatly simplified in many cases of absorption since then the lower electronic level is usually in a low state of vibrational excitation and may therefore be quite accurately represented by a harmonic wave function. In this case the expression becomes

$$I_{v'v''} = \sum_{k=v'-4}^{v'+4} C_{v'k} I_{kv''}^{0} \tag{13}$$

which contains only nine terms.

III. Application to Hydrogen Absorption Bands

There are no absorption spectrum measurements which are precise enough to determine how nearly Eq. (12) represents reality for the intensities of vibrational electronic bands. However, to see what changes are introduced by removing the restriction of linear oscillations, computations are carried out for hydrogen. Hydrogen is especially suitable because at room temperatures nearly all of the molecules are in the first vibrational level so that the distribution factor does not enter into the intensity calculations and furthermore Eq. (13) instead of Eq. (12) may be quite accurately applied.

In order to have some comparison between the calculated and observed results the experimentally estimated intensities are given in Table I. They are taken from Schaafsma and Dieke[5] and differ somewhat from those given in Part I. Estimated intensities are given for each rotational transition and show the hopelessness of exact comparisons between theory and experiment. Schaafsma and Dieke especially emphasize the difficulty of making intensity estimates for hydrogen due to the strength of the continuous spectrum in that region.

The constants used in the harmonic oscillator calculations are:

$\omega_e' = 1357.3$	$r_e' = 1.300$	$\alpha = 0.557$
$\omega_e'' = 4376.0$	$r_e'' = 0.750$	$\delta = -0.209$

where α and δ are the constants in Eq. (13) of Part I. These values differ somewhat from the more recent values given by Hyman[6] but small changes in these constants will not change the calculated intensities very much.

[4] The constant term C_3 is given wrong on page 415 of Part I. It should read $[2/\alpha(1+\alpha^2)]^{1/2} e^{-\delta^2/2(1+\alpha^2)}$. This factor is the same for all transitions and therefore has no effect on the value of the relative intensities.

[5] A. Schaafsma and G. H. Dieke, Zeits. f. Physik **55**, 164 (1929).

[6] H. H. Hyman, Phys. Rev. **36**, 187 (1930).

TABLE I. *Intensities in hydrogen absorption.*

Rotational Transition	A_0-B_0	A_0-B_1	A_0-B_2	A_0-B_3	A_0-B_4	A_0-B_5	A_0-B_6	A_0-B_7	A_0-B_8	A_0-B_9
A. Experimental (Schaafsma and Dieke)										
R(0)	0	3	4	2	2	4	1	3	2	3
R(1)	2	3	4	3	2	4	2	3	2	3
R(2)						4	1	3	2	
R(3)				0	0	0	1	1	1	
R(4)								0		
P(1)	2	3	4	5	4	4	2	3	2	3
P(2)	2	2		0	00	0	1	1	1	
P(3)	2	2		0	00	0		0		
B. Calculated										
Harmonic Oscillations	1.00	7.19	22.2	37.7	37.0	19.4	3.58	0.05	1.32	0.03
Perturbation Theory	1.00	6.6	14.1	5.2	4.7	27.4				
Morse's Function	1.00	4.28	10.7	15.5	16.4	12.5	6.96			

The above table gives the estimated relative intensities of many lines in the H_2 absorption bands which have a common initial level A_0. Below are given the corresponding calculated intensities obtained from three different approximations. The occurrence of many gaps in the experimental part of this table is probably due to the intensity of the continuous spectra in this region.

To determine the coefficients in the power series expansion of the potential energy, formulas may be derived if one assumes the relation between the total energy and the quantum numbers as given by Fues.[2] If the potential energy is given by

$$U(\xi) = k(\xi^2 + c_3\xi^3 + c_4\xi^4)$$

we have

$$k = 0.1774 \cdot 10^{-11}\omega_e^2 J_e \text{ ergs}$$
$$c_3 = -(0.2179\alpha'\omega_e J_e^2 + 1)$$
$$c_4 = 1.250c_3^2 - 2.410\omega_e x J_e$$

where α and x are the band spectra constants occurring in the expression for energy as a function of the quantum numbers; (the prime on the α' is used merely to distinguish it from α used in Part I). We then obtain for the potential energy expansions[7]

$$U'(\xi) = 0.459(\xi^2 - 1.560\xi^3 + 2.380\xi^4) \times 10^{-11} \text{ ergs}$$
$$U''(\xi) = 1.587(\xi^2 - 1.561\xi^3 + 1.770\xi^4) \times 10^{-11} \text{ ergs}$$

in which the following constants are used

$$J_e' = 1.404 \times 10^{-40} \text{ gm cm}^2 \qquad \alpha' = 0.96 \text{ cm}^{-1} \qquad \omega_e'x' = 19.54 \text{ cm}^{-1}$$
$$J_e'' = 0.467 \times 10^{-40} \text{ gm cm}^2 \qquad \alpha'' = 2.7 \text{ cm}^{-1} \qquad \omega_e''x'' = 113.5 \text{ cm}^{-1}.$$

[7] These expressions are approximately the same as those given by O. W. Richardson and P. M. Davidson, Proc. Roy. Soc. **A125,** 23 (1929) in which higher powers are included.

From the values of c_3 and c_4 obtained above for U' the coefficients in Eq. (13) are calculated and finally the values given in the table are obtained.

It is desirable to obtain analytical expressions for the intensities calculated by using the wave functions derived from the potential energy given by Morse.[8] The writer has been unable to carry through the necessary integrations in this case. However in order to determine the effect of assuming such a potential function the integrations were carried out graphically and the results are given in Table I. The potential energy function in this case has the form:

$$U(\xi) = D(e^{-2ar_0\xi} - 2e^{-ar_0\xi})$$

where $D = c\omega_e^2 h/4\omega_e x$ and $a = (8\pi^2\mu c\omega_e x/h)^{1/2}$. The same band spectrum constants are used in this case as before. The fundamental constants are taken from Birge.[9]

It is apparent from Table I that the extremely high intensities given by the harmonic oscillator calculations are reduced in both of the more exact calculations in agreement with experiment. The power series calculations are only given as far as the transition $B_5 - A_0$ since even for the last two given the perturbations are so large that scarcely any faith can be placed in the results. When the coefficients c_3 and c_4 in the power series expansion are large as they are in hydrogen, the perturbation theory, even when carried out to two approximations, gives reliable results only for transitions between the lowest vibrational quantum levels.

The calculations based upon Morse's potential energy function are probably more accurate than those using the perturbation theory. This is partly due to the fact that the "A" level as well as the "B" level is corrected for deviations from simple harmonic oscillations. It is probable also that Morse's function approaches reality nearer than a three term power series for the higher transitions. Higher calculations than those given involve small differences between large quantities and are therefore subject to large errors.

These calculations were carried out at the University of Michigan and the writer wishes to express his gratitude to Professor H. M. Randall for the opportunity of spending an extremely interesting and profitable summer in Ann Arbor. The writer wishes also to thank Professor Ruark of the University of Pittsburgh for many helpful suggestions in the preparation of the manuscript.

Note added in proof: J. L. Dunham (Phys. Rev. **36,** 1553 (1930)) has pointed out that since the electric moment does not change nearly as rapidly as the eigenfunctions, the results of Part I and hence Part II, do not need to be restricted to symmetrical molecules for small quantum numbers. The correction given in footnote 4 is noted in his article also.

[8] P. M. Morse, Phys. Rev. **34,** 57 (1929).
[9] R. T. Birge, Reviews of Modern Physics **1,** 1 (1929).

DERIVATION OF HYPERFINE STRUCTURE FORMULAS FOR ONE ELECTRON SPECTRA

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Abstract

A short but rigorous derivation is given for the energy level separations caused by a nuclear magnetic moment in a one electron spectrum. Formulas (5) and (7) are general. For weak coupling between the orbital angular momentum and the electron spin formula (6) may be used.

FORMULAS for the hyperfine structure of one electron spectra have been derived by numerous authors.[1] The calculations are in most cases very lengthy and are carried out for special cases. The results may be obtained by the following short and yet rigorous consideration. The interaction energy of a nucleus with an electron of charge $-e$ may be represented by

$$H' = g\mu_0(\mathbf{A}\cdot\mathfrak{y}) \tag{1}$$

where $\mathfrak{y}$ is the angular momentum matrix vector of the nucleus in units $h/2\pi$ and $g\mu_0\mathfrak{y}$ is its magnetic moment. μ_0 is the Bohr magneton and g is a numerical factor to be determined by comparison with experiment. Here

$$\mathbf{A} = 2\mu_0[r^{-3}\mathbf{L} - \boldsymbol{\sigma}r^{-3} + 3\mathbf{r}(\mathbf{r}\boldsymbol{\sigma})r^{-5}]/[1 + (eA_0/2mc^2)] + 2\mu_0[\boldsymbol{\sigma}r^{-2} - \mathbf{r}(\mathbf{r}\boldsymbol{\sigma})r^{-4}]\frac{d}{dr}[1 + (eA_0/2mc^2)]^{-1} \tag{2}$$

$\mathbf{L}$ is the orbital angular momentum in units $h/2\pi$, $2\boldsymbol{\sigma}$ is Pauli's spin vector so that $(h/2\pi)\boldsymbol{\sigma}$ is the angular momentum of the electron spin, r is the distance from the nucleus and A_0 is the electrostatic potential. Expression (2) may be derived from the Dirac equation by eliminating two wave functions. The first part of (2) is the only important one except for s terms where the second part is responsible for all of the effect. The total angular momentum is

$$\mathbf{F} = \mathbf{J} + \mathfrak{y} = \mathbf{L} + \boldsymbol{\sigma} + \mathfrak{y}. \tag{3}$$

The quantum number of $\mathbf{F}$, $\mathbf{J}$, $\mathbf{L}$, $\mathfrak{y}$ we write as f, j, l, i. By well-known theorems about angular momenta we have for the perturbed energy

$$w = g\mu_0(\mathbf{AJ})_j[f(f+1) - i(i+1) - j(j+1)]/[2j(j+1)]. \tag{4}$$

Here $(\mathbf{AJ})_j$ is the value of any diagonal element in the matrix $(\mathbf{AJ})$ in that part of it which belongs to the quantum number j. Substituting $\mathbf{J}=\mathbf{L}+\boldsymbol{\sigma}$ into $(\mathbf{AJ})$ we have except for s terms

[1] J. Hargreaves, Proc. Roy. Soc. **124**, 568 (1929); **127**, 141, 407 (1930). E. Fermi, Zeits.f. Physik **60**, 320 (1930). Unpublished calculations of Casimir quoted in Pauling and Goudsmit's book.

$$(\boldsymbol{AJ})/2\mu_0 = -\boldsymbol{\mathfrak{s}}^2 r^{-3} + 3(\boldsymbol{r}\boldsymbol{\mathfrak{s}})^2 r^{-5} + 3(\boldsymbol{rL})(\boldsymbol{r}\boldsymbol{\mathfrak{s}})r^{-5} + r^{-3}\boldsymbol{L}^2.$$

The denominator of the first part of (2) being set here $=1$ since $eA_0/2mc^2$ is in this case small. We note that $\boldsymbol{rL}=0$ and that $3(\boldsymbol{r}\boldsymbol{\mathfrak{s}})^2 - r^2\boldsymbol{\mathfrak{s}}^2 = 0$. We have then

$$w = g\mu_0{}^2(r^{-3}\boldsymbol{L}^2)_{,}[f(f+1) - i(i+1) - j(j+1)]/[j(j+1)]. \qquad (5)$$

This is exact since the coupling to the nucleus is weak. If in addition the coupling of $\boldsymbol{L}$ and $\boldsymbol{\mathfrak{s}}$ is weak we may write $\boldsymbol{L}^2 = l(l+1)$ so that

$$w = g\mu_0{}^2\frac{l(l+1)}{j(j+1)}[f(f+1) - i(i+1) - j(j+1)]\overline{(r^{-3})} \qquad (6)$$

For s terms the denominator $1+(eA_0/2mc^2)$ insures the disappearance of the first part of (2) in the approximation of formula (5). In this case

$$(\boldsymbol{AJ})_j = 2\mu_0\int_0^\infty \psi^2(r)(1/2r^2)\left\{\frac{d}{dr}[1 + (eA_0/2mc^2)]^{-1}\right\}4\pi r^2 dr \cong 4\pi\mu_0\psi^2(0) \qquad (6')$$

in the same approximation as Fermi's.[2] If therefore we add to (6) the statement that for $l=0$

$$[\overline{(r^{-3})}l(l+1)]_{l=0} = 2\pi\psi^2(0) \qquad (7)$$

formula (6) becomes complete.

These results in the approximation of equation (6) are in complete agreement with the statements made in Pauling and Goudsmit's book where the calculations of Casimir have been used.

[2] The exact formula for a Coulomb field is found in G. Breit Phys. Rev. **35, 1447 (1930).**

THE DIFFRACTION OF AN ELECTRON-WAVE AT A SINGLE LAYER OF ATOMS

By M. v. Laue*

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Abstract

This paper undertakes to estimate the influence of the gradual transition between the field exterior to, and in the interior of a crystal, on the diffraction of electrons. This gradual transition is required by electrostatics. The result is, that this influence may be neglected for electrons whose energy is two hundred volts or more. One can then treat the transition as discontinuous. In the case of slower electrons it seems doubtful, if such a treatment is permissible.

Introduction

THE theory of the diffraction of electrons by a space-lattice has been discussed by Bethe and later, under simplifying assumptions by Morse.[1] These authors integrate the Schrödinger-equation for the internal field in so complete a manner, that little more is to be said. Their treatment of the incidence and reflection at the surface cannot be considered as equally satisfactory. They treat the triply periodic internal field as though it ceases suddenly at a certain plane. This is in complete contradiction to electrostatics, as one may not consider this plane as charged without coming into conflict with the atomistic foundations of the whole theory. The field certainly dies off asymptotically as one proceeds outward. This is doubtless a lack in the theory which, as it seems to us,—might cast doubt on its applicability to the experiments. At least it should be examined to see if and under what circumstances this approximation is justifiable. As a matter of fact it will appear that this is not always the case.

Properly one should treat the atoms as having a finite extension but then the calculations based on the Schrödinger-equation would encounter a difficulty which is only too well known in optics, namely the reflection and refraction at a plane plate with continuously variable refractive index. Of necessity, then, we will treat the atoms as point charges. The order of magnitude of our results will probably not be influenced.

To obtain a comparison let us glance at the theory of Röntgen-interference which is similar to Bethe's in many points. In this treatment one considers the space-lattice of diffracting centers to be bounded by a definite lattice-plane; one can also object to this since the atoms in the boundary planes actually do not occupy exactly the position which they would have if the crystal were continued beyond the boundary. But since a single layer of atoms contributes very little to the resultant intensity of Röntgen-rays this

* Translated from the German by C. Eckart.

[1] H. Bethe, Ann. d. Physik **87**, 55 (1928); P. M. Morse, Phys. Rev. **35**, 1910 (1930).

assumption can have little influence. In the case of electron-diffraction things are essentially different.

Let the primitive periods of the lattice-plane be the vectors $\mathfrak{a}_1$ and $\mathfrak{a}_2$; the reciprocal vectors $\mathfrak{b}_1$, $\mathfrak{b}_2$ which lie in the same plane are defined by the equations

$$(\mathfrak{a}_1\mathfrak{b}_1) = 1,\ (\mathfrak{a}_1\mathfrak{b}_2) = 0,\ (\mathfrak{a}_2\mathfrak{b}_1) = 0,\ (\mathfrak{a}_2\mathfrak{b}_2) = 1. \tag{1}$$

The surface-density of electricity in this plane will be

$$\rho = \sum_1 \rho_m e^{2\pi i(\mathfrak{b}_m \mathfrak{r})} \tag{2}$$

where $\mathfrak{r}$ is the vector drawn from an arbitrary origin in the lattice-plane to the point of consideration, and

$$\mathfrak{b}_m = m_1\mathfrak{b}_1 + m_2\mathfrak{b}_2. \tag{3}$$

The coefficient ρ_0 is zero, since the total charge must vanish. The other coefficients are given by the equation

$$\rho_m = \frac{1}{F}\int \rho e^{-2\pi i(\mathfrak{b}_m \mathfrak{r})} d\sigma,$$

in which F is the area of the parallelogram subtended by $\mathfrak{a}_1$, $\mathfrak{a}_2$, and the integration is to be extended over such a parallelogram. If a positive pole of charge Z lie at $\mathfrak{r}_+ = \delta_1\mathfrak{a}_1 + \delta_2\mathfrak{a}_2$ a negative pole of the same strength at $\mathfrak{r}_- = -(\delta_1\mathfrak{a}_1 + \delta_2\mathfrak{a}_2)$ then according to 1):

$$\rho_m = -\frac{2Z\epsilon}{F} i \sin 2\pi(m_1\delta_1 + m_2\delta_2). \tag{4}$$

We assume that the lattice plane has the equation $z = 0$. Then these charges produce the potential

$$\phi = \sum \phi_m e^{2\pi i(\mathfrak{b}_m \mathfrak{r})} e^{-2\pi |\mathfrak{b}_m| |z|} \tag{5}$$

in which[2]

$$\phi_m = \frac{\rho_m}{|\mathfrak{b}_m|}. \tag{6}$$

The coefficient ϕ_0 vanishes. It would have to be—because of $\Delta\phi = 0$—a linear function of z and this must vanish because of the boundary conditions at $z = \pm\infty$.

It would be otherwise if we had, e.g., two parallel planes of which the one had a net positive charge, the other an equal negative: then ϕ_0 would be different from zero between the two planes. Also if the atoms were not taken to be point-charges there would be regions in which ϕ_0 did not vanish.

[2] This series is naturally double. The index m represents the pair of indices m_1 and m_2 which occur in (3) explicitly.

The Schrödinger-equation of the free electron

$$\Delta\psi + \frac{8\pi^2\mu}{h^2}E\psi = 0$$

is integrated by the function

$$\psi = e^{2\pi i(\boldsymbol{K}_0\boldsymbol{R})}, \quad (\boldsymbol{K}_0) = \frac{1}{h}(2\mu E)^{1/2} \tag{7}$$

in which $\boldsymbol{R}$ is the three-dimensional vector to the point under consideration (Aufpunkt); $\boldsymbol{r}$ is the component of $\boldsymbol{R}$ parallel to the plane $z=0$, μ the mass of electron. We also resolve the vector $\boldsymbol{K}_0$ into a component $\boldsymbol{k}_0$ parallel to this plane and one parallel to the z axis—z the magnitude of the latter is $\kappa_0 = (\boldsymbol{K}_0^2 - \boldsymbol{k}_0^2)^{1/2}$. Then Eq. (7) becomes

$$\psi = \psi_0(z)e^{2\pi i(\boldsymbol{k}_0\boldsymbol{r})}, \quad \psi_0(z) = e^{2\pi i\kappa_0 z} \tag{8}$$

We assume that κ_0 is positive; the wave than proceeds from positive to negative z-values.

The Schrödinger-equation of the electron as perturbed by the lattice-plane

$$\Delta\psi + \frac{8\pi^2\mu}{r^2}(E - \epsilon\phi)\psi = 0$$

we attempt to resolve in the form

$$\psi = \sum\psi_m(z)e^{2\pi i(\boldsymbol{k}_0+\boldsymbol{b}_m,\boldsymbol{r})}.$$

It then reads

$$\Delta\psi = \sum\left(\frac{d^2\psi_m}{dz^2} - 4\pi^2(\boldsymbol{k}_0 + \boldsymbol{b}_m)^2\psi_m\right)e^{2\pi i(\boldsymbol{k}_0+\boldsymbol{b}_m,\boldsymbol{r})} \tag{9}$$

from which we can cancel the factor $e^{2\pi i\boldsymbol{k}_0\boldsymbol{r}}$. The remaining equation is then:

$$\sum_m\left(\frac{d^2\psi_m}{dz^2} + 4\pi^2(\boldsymbol{K}_0^2 - (\boldsymbol{k}_0 + \boldsymbol{b}_m)^2)\psi_m\right)e^{2\pi i(\boldsymbol{b}_m\boldsymbol{r})}$$

$$= \frac{8\pi^2\epsilon\mu}{h^2}\sum_{p,q}\psi_p(z)\phi_q e^{-2\pi|\boldsymbol{b}_q||z|}e^{2\pi i(\boldsymbol{b}_q+\boldsymbol{b}_q,\boldsymbol{r})}$$

According to Eq. (3)

$$\boldsymbol{b}_p + \boldsymbol{b}_q = \boldsymbol{b}_{p+q}.$$

Since this equation must be true for every value of the vector $\boldsymbol{r}$, the separate terms on each side which have the same exponential factor must be identical, i.e.

$$\frac{d^2\psi_m}{dz^2} + 4\pi^2(\boldsymbol{K}_0^2 - (\boldsymbol{k}_0 + \boldsymbol{b}_m)^2)\psi_m = \frac{8\pi^2\epsilon\mu}{h^2}\sum_p\psi_p(z)\phi_{m-p}e^{-2\pi|\boldsymbol{b}_{m-p}||z|} \tag{10}$$

To solve this system of infinitely many differential-equations with infinitely many unknowns $\psi_m(z)$ we use a method of approximation. As first approximation one will substitute for ψ_0 the value (8) of the wave-function of the unperturbed incident wave, and retain only the term in ψ_0 on the right side of (10). The weaker the intensity of the diffracted waves comes out, the better will be this approximation. Since $\phi_0 = 0$ we then obtain the equation:

$$\frac{d^2\psi_m}{dz^2} + 4\pi^2(\boldsymbol{K}_0^2 - (\boldsymbol{k}_0 + \boldsymbol{b}_m)^2)\psi_m = \frac{8\pi^2\epsilon\mu}{h^2}\psi_0(z)\phi_m e^{-2\pi|b_m||z|} \tag{11}$$

of which the solution satisfies the condition that it must represent *emergent* waves at $z = \pm\infty$ is

$$\psi_m(z) = 2\pi i\frac{\epsilon\mu}{h^2}\frac{\phi_m}{\epsilon_m}\Big\{e^{2\pi i\epsilon_m z}\int_z^\infty \psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{-2\pi i\epsilon_m\zeta}d\zeta + e^{-2\pi i\epsilon_m z}\int_{-\infty}^z \psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{+2\pi i\epsilon_m\zeta}d\zeta\Big\}. \tag{12}$$

The abbreviation

$$\epsilon_m = (\boldsymbol{K}_0^2 - (\boldsymbol{k}_0 + \boldsymbol{b}_m)^2)^{1/2} \tag{13}$$

has been used. That this is a solution of Eq. (11) will be seen on substitution. For $z = +\infty$ we obtain from (12):

$$\psi_m = 2\pi i\frac{\epsilon\mu}{h^2}\frac{\phi_m}{\epsilon_m}e^{-2\pi i\epsilon_m z}\int_{-\infty}^{+\infty}\psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{+2\pi i\epsilon_m\zeta}d\zeta \tag{14}$$

At $z = -\infty$ correspondingly

$$\psi_m = 2\pi i\frac{\epsilon\mu}{h^2}\frac{\phi_m}{\epsilon_m}e^{+2\pi i\epsilon_m z}\int_{-\infty}^{+\infty}\psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{-2\pi i\epsilon_m\zeta}d\zeta. \tag{15}$$

These are the emergent waves required by the boundary conditions, at least, if ϵ_m is real and positive.

The latter may always be assumed to be the case, as the sign is not defined by (13). The former is not always true according to (13). In addition to the diffracted homogeneous waves there are also inhomogeneous ones which are propagated along the lattice-plane and die off asymptotically in a direction perpendicular to this plane. For every pair with indices m with real ϵ_m there are always two emergent waves on each side of the lattice-plane.

It will be remarked that Eq. (12) is still valid for such index pairs, m, for which $i\epsilon_m$ is positive and real.[3] If one draws the factor $e^{\pm 2\pi i\epsilon_m z}$ under the integral sign, than the bracket in (13) has the value

$$\int_z^\infty \psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{2\pi i\epsilon_m(z-\zeta)}d\zeta + \int_{-\infty}^z \psi_0(\zeta)e^{-2\pi|b_m||\zeta|}e^{-2\pi i\epsilon_m(z-\zeta)}d\zeta$$

[3] Negative real values may be left out of account since the sign of the root in (13) is arbitrary; they must be left out of account, because Eq. (12) is not longer valid when $i\epsilon_m < 0$.

in the first of these integrals $z-\zeta$ is negative, in the second positive. They both exist therefore. Only Eqs. (14) and (15) must be changed for this case; but our interest is only for the homogeneous waves, i.e., real values of ϵ_m.

For the justification of this calculation it is essential that Eq. (11) applied to the index pair 0,0 possesses the solution $\psi_0(z)$ as given in Eq. (8). This would not be the case, if ϕ_0 did not vanish. In that case we would encounter the problem of the plane parallel plate as remarked in the introduction and would have to use its solution in evaluating the other ψ_m.

The integrals in (14) and (15) are to be evaluated for real values of ϵ_m and ψ_0 as in (8). They are

$$\int_{-\infty}^{+\infty} e^{2\pi i(\kappa_0 \pm \epsilon_m)\zeta} e^{-2\pi|b_m||\zeta|} d\zeta$$

$$\int_0^{\infty} e^{2\pi i(\kappa_0 \pm \epsilon_m)\zeta} e^{-2\pi|b_m|\zeta} d\zeta + \int_{-\infty}^{0} e^{2\pi i(\kappa_0 \pm \epsilon_m)\zeta} e^{+2\pi|b_m|\zeta} d\zeta$$

$$= 2\int_0^{-\infty} \cos\,(2\pi(\kappa_0 \pm \epsilon_m)\zeta) e^{-2\pi|b_m|\zeta} d\zeta = \frac{1}{\pi} \frac{|b_m|}{(\kappa_0 + \epsilon_m)^2 + b_m{}^2}$$

If we now use the value of ϕ_m given by (6) and ρ_m given by (4), we obtain

$$\psi_m(z) = \frac{4Z\epsilon^2\mu}{h^2} \frac{\sin 2\pi(m_1\delta_1 + m_2\delta_2)}{F} \frac{e^{\mp 2\pi i\epsilon_m z}}{\epsilon_m[(\kappa_0 \pm \epsilon_m)^2 + b_m{}^2]} \text{ for } z = \pm\infty \quad (16)$$

in which the abbreviations

$$\kappa_0 = (K_0{}^2 - k_0{}^2)^{1/2} = |K_0| \cos\theta, \quad |K_0| = \frac{1}{h}(2\mu E)^{1/2}$$

$$\epsilon_m = (K_0{}^2 - (k_0 + b_m)^2)^{1/2} = (K_0{}^2 \cos^2\theta - 2(k_0 b_m) - b_m{}^2)^{1/2}$$

have been used. The angle θ is the angle of incidence of the original electron wave. Only the last of the three fractions in (16) depends on the energy of the electrons, and it diminishes with increasing E approximately as $E^{-3/2}$. For sufficiently fast electrons the amplitude of every ψ_m-wave is so small, that the diffracting-power of the single atomic layer is insignificant. The neglect of the surface layers is then justified. To obtain an estimate of the lower limit above which this is true we will later evaluate Eq. (16) numerically.

One can best estimate the strength of an inhomogeneous wave if one determines its amplitude in the lattice-plane itself ($z=0$). We designate the real positive quantity $i\epsilon_m$ by η_m. From (12), (6) and (4) it then follows without difficulty that:

$$\psi_m(0) = \frac{4Z\epsilon^2\mu}{h^2} i \sin 2\pi(m_1\delta_1 + m_2\delta_2) \frac{|\boldsymbol{b}_m| + \eta_m}{|\boldsymbol{b}_m|(\eta_m)[(\boldsymbol{b}_m + \eta_m)^2 + \kappa_0^2]}.$$

One notices the diminution of the amplitude with increasing indices m_1, m_2.

For numerical purposes we suppose the vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ perpendicular the one to another and both of length 4×10^{-8} cm. Then the reciprocal vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ will also be perpendicular and of the magnitude 2.5×10^{7} cm^{-1}. In each square formed by $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ we suppose one positive and one negative charge—each of $Z=1$, but we do not determine their positions more definitely, i.e., the numbers δ_1, δ_2 are thus undetermined. Then the first factor in (16) is

$$\frac{4\epsilon^2\mu}{h^2F} = 1.25\times 10^{22}\ \text{cm}^{-3}.$$

We suppose an electron beam of 150 volts energy to be incident normally on this lattice plane. The de Broglie wave-length is 10^{-8} cm, also $\kappa_0 = |\boldsymbol{k}_0| = 10^{8}$ cm^{-1}. Then only those homogeneous waves can appear, for which the indices m_1, m_2 are any combination of the numbers ± 1 and 0. This results in 8 emergent beams from each side of the lattice plane. If one index is 0, the other ± 1 Eq. (16) gives

$$\frac{|\psi|^2_{z=+\infty}}{\sin^2(2\pi(m_1\delta_1 + m_2\delta_2))} = 10^{-5}, \quad \frac{|\psi|^2_{z=-\infty}}{\sin^2(2\pi(m_1\delta_1 + m_2\delta_2))} = 4\times 10^{-2}$$

If both indices are ± 1, then one finds

$$\frac{|\psi|^2_{z=+\infty}}{\sin^2(2\pi(m_1\delta_1 + m_2\delta_2))} = 1.5\times 10^{-5}, \quad \frac{|\psi|^2_{z=-\infty}}{\sin^2(2\pi(m_1\delta_1 + m_2\delta_2))} = 3\times 10^{-3}$$

$\sin^2(\ )$ is the structure factor and obviously depends on the position of the two pointcharges in the elementary parallelogram. Since we set the intensity of the incident wave equal to 1, the foregoing numbers represent the relative intensity of the diffracted rays. As they are small compared with 1, one will conclude firstly, that the present approximation is sufficient, and secondly, that the diffracting-power of the single plane is so small that it is justified to neglect the surface fields as Bethe and Morse have done.

The result is quite different if we consider electrons of energy 37.5 volts, other things remaining the same (wave-length $\lambda = 2\times 10^{-8}$ cm). Then the only possible homogeneous waves are those for which one index is 0, the other ± 1. At $z=+\infty$ the fraction $|\psi|^2/\sin^2(\ )$ has a sufficiently small value, namely 10^{-3}; but for $z=-\infty$ it becomes even greater than 1, which naturally means that the present approximation is useless. In this case it seems that space lattice theories of Bethe and Morse require extension by considerations regarding the surface layers.

In summary we may safely say, despite the fact that the case here considered is far from the real one, that for electrons of 200 or more volts energy

the neglect of the surface action in the space lattice theory of electron diffraction is justified, but that this is not obviously true at smaller velocities.

In the experiments of Stern and his collaboraters on the diffraction of atoms and molecules by crystals, the plane-grating-action of the surface is the only thing observed, no space-lattice effects. The theory of these phenomena one must probably attempt to carry through in a similar manner to the above. The essential difference will be in a different value of the coefficients ϕ_m of the Fourier-series for the potential energy. The form (9) for the wave-function and the approximation introduced in (11) may probably be retained.

SOME PHOTOELECTRIC AND THERMIONIC PROPERTIES OF RHODIUM

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Abstract

A thin ribbon of rhodium was subjected to rigorous heat treatment at 950°–1450°C for 1050 hours in a final vacuum of 10^{-8} mm of Hg in order to put it in a stable condition for photoelectric and thermionic measurements. During this period the long wave limit shifted from about 2530A to 3150A and then shifted back to 2509A where it remained during the latter 375 hours of heat treatment.

The photoelectric current was found to increase about 130% as a result of increasing the temperature of the rhodium from 25°C to 950°C. A rather sudden increase took place at about 240°C.

The photoelectric work function at 25°C was determined from the final long wave limit of 2482–2536A to be 4.92 ± 0.06 volts. The long wave limit at 240°C was 2652–2752A which gave a photoelectric work function of 4.57 ± 0.09 volts for this temperature. No further change in long wave limit was observed up to 650°C.

An anomaly was observed at 1100°C where the thermionic current was irregular and where the rate of change of the resistance of the rhodium with temperature changed on increasing the temperature.

The thermionic work function of rhodium, as determined from observations and with Richardson's equation, was 4.58 ± 0.09 volts. This value agrees with the photoelectric work function at 240°C.

Pure hydrogen and oxygen were introduced separately into the experimental tube while the rhodium was in its outgassed equilibrium condition. In the case of hydrogen the wave limit was changed from 2482–2536A to 2378–2482A. In the case of oxygen the wave limit was changed from 2482–2536A to a value so low that it could not be determined by the method used in this work.

AMONG the photoelectric and thermionic studies of metals which have been subjected to rigorous heat treatment, or distillation, there are: DuBridge's[1] extensive study of the thermionic and photoelectric properties of platinum; Cardwell's[2] work with iron and cobalt; Martin's[3] thermionic and photoelectric study of molybdenum; Warner's[4] work with tungsten; the work of Kazda,[5] Dunn,[6] and Hales[7] on mercury; and Goetz's[8] study of tin.

The object of this investigation has been (1) to investigate the photoelectric and thermionic properties of rhodium during and after subjection

[1] DuBridge, Nat. Acad. Sci. **12,** 162 (1926); Phys. Rev. **31,** 236 (1928); Phys. Rev. **32,** 961 (1928).
[2] Cardwell, Nat. Acad. Sci. **14,** 439 (1928); Nat. Acad. Sci. **15,** 544 (1929).
[3] Martin, Phys. Rev. **33,** 991 (1929).
[4] Warner, Nat. Acad. Sci. **13,** 56 (1927); Phys. Rev. **33,** 815 (1929).
[5] Kazda, Phys. Rev. **26,** 643 (1925).
[6] Dunn, Phys. Rev. **29,** 693 (1927).
[7] Hales, Phys. Rev. **32,** 950 (1928).
[8] Goetz, Phys. Rev. **33,** 373 (1929).

to rigorous heat treatment and (2) to introduce known gases in order to determine their effects upon the photoelectric properties of rhodium in the outgassed condition.

Apparatus

The experimental tube was similar to that used by DuBridge[9] with a few exceptions. Charcoal was not used in this work. Potential leads, spot-welded about a quarter of an inch below the ends of the filament, permitted the measurement of the P. D. across the filament. A grounded guard ring was installed between the collecting cylinder lead and all of the other leads of the experimental tube. The fact that Pyrex was sufficiently conducting at 100° C to prevent an accurate measurement of the photoelectric current immediately after cutting off the heating current made this device compulsory. The rhodium, purchased from the American Platinum Works, Newark, N. J. in the purest state that they could furnish, was in the form of ribbons 10 cm long by 0.4 cm wide by 0.004 cm thick. Each ribbon, bent in the form of a loop, was suspended inside a molybdenum collecting cylinder from two fifty mil tungsten leads through which current could be sent to heat the specimen to any desired temperature. All of these devices were enclosed in a Pyrex tube which was connected through two liquid air traps, a mercury cut-off, and a water-cooled mercury diffusion pump to a "Cenco" fore pump. The molybdenum cylinder was provided with two one half inch holes, one for illuminating the specimen and the other for pyrometric measurements of the temperature. A shutter, operated by an external magnet, could cover the opening through which the photo-active light had to pass. A quartz window, attached to the experimental tube by means of a graded quartz-Pyrex seal, served to admit radiation from a Cooper-Hewitt quartz mercury arc which was operated by a current of 3.1 amperes. The vertical arc was enclosed in a metal housing. Pressures lower than 10^{-6} mm of Hg were measured with an ionization manometer which was calibrated by extrapolating from data obtained by means of a McLeod gauge. The extrapolation was based on the work of Dushman and Found.[10] The photoelectric currents due to the full radiation of the mercury arc were measured by means of a Compton[11] electrometer shunted with a resistance of 10^9 ohms, thus permitting the use of the steady deflection method of measuring current. The sensitivity of the electrometer was determined at the time of each observation. The rate of charge method of detecting current was used in getting the long wave limit.

Outgassing Treatment

For 48 hours the molybdenum collecting cylinder was heated by electron bombardment in an auxiliary vacuum system at 800–1000°C before it was introduced into the experimental tube. When the experimental vacuum system was apparently free from leaks and the pressure was as good as could

[9] DuBridge, Phys. Rev. **29**, 451 (1927).
[10] Dushman and Found, Phys. Rev. **23**, 734 (1924).
[11] Compton, Phys. Rev. **14**, 85 (1919).

be read on the McLeod guage (of the order of 10^{-7} mm of Hg), the ionization manometer, the experimental tube, and the second liquid air trap were heated for 94 hours at approximately 400, 500, and 500 degrees C respectively. At the end of this period the pressure was again of the order of 10^{-7} mm of Hg while the tubes were hot. Then, in order to avoid excessive evaporation of the specimen, it was heated by a current at temperatures which were gradually increased from about 900°C to 1250°C and finally to 1450°C. The high vacuum end of the system up to the first liquid air trap was heated with a torch.

Fatigue

In Fig. 1 the photoelectric current due to the full arc is plotted as a function of the time of rest after cutting off the heating current. After fifty hours heating of the specimen there is a marked fatigue which becomes more pronounced until 250 hours of heating. Then it becomes rapidly less marked until

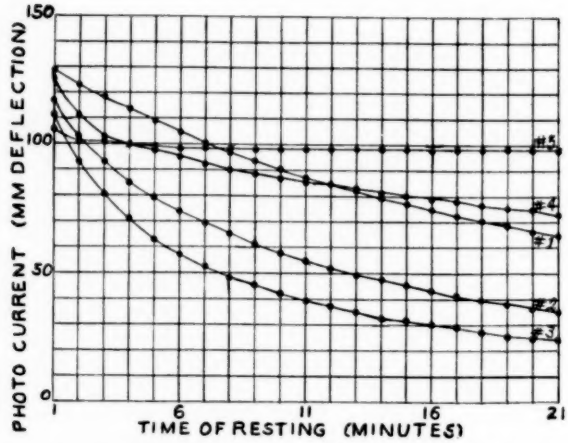

Fig. 1. Decrease of photoelectric sensitivity with time, using full arc.
Curve #1, taken after 50.5 hours of heat treatment.
Curve #2, " " 116.5 " " " "
Curve #3, " " 250.5 " " " "
Curve #4, " " 276.9 " " " "
Curve #5, " " 372.2 " " " "

there is practically no fatigue except for the first four or five minutes after cutting off the heating current. The drop in sensitivity during this short interval can be reasonably attributed to the fact that it required four or five minutes for the filament to cool to approximately room temperature. That this is the probable cause of the rapid initial change was shown by correlating the rate of cooling of the filament, as determined from resistance measurements, with the temperature change of photo-sensitivity. In determining a fatigue curve the first photoelectric observation was taken one minute after the heating current was stopped, and from the above mentioned comparison it was concluded that the filament was at this instant at a temperature of about 240°C. The change in the photo-current during the next

few minutes is associated with a phenomenon discussed in the next paragraph.

Variation of Photoelectric Sensitivity with Temperature

Rhodium, like Pt, Co, W, and Fe in the γ form, has a positive temperature coefficient after it has been subjected to severe outgassing conditions. There is an increase of 130% in the photoelectric current in going from room

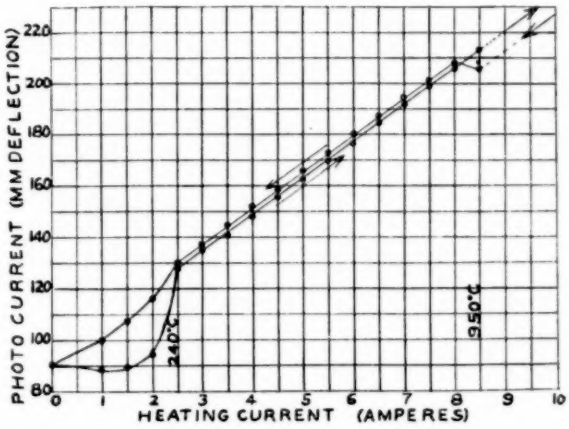

Fig. 2. Total photo-current as a function of heating current.

temperature to a temperature of 950°C. In Fig. 2 the photoelectric current due to the full arc is plotted as a function of the heating current. The temperature was decreased slowly from 1100°C to 950°C and then readings were taken as indicated in Fig. 2. The data for this curve were taken after the filament had been heated for 640 hours at approximately 1250°C. The pressure was 10^{-8} mm of Hg. For each reading five minutes were allowed for

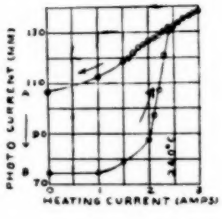

Fig. 3.

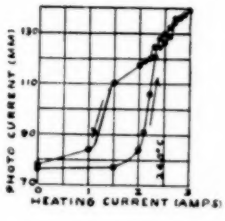

Fig. 4.

attaining temperature equilibrium. The photo-current variation with temperature between 240°C and 950°C can be reproduced without serious difficulty. The difference between the two curves in Fig. 2 between 240°C and 950°C is due to the fact that the specimen was cooled slowly from 1100°C where rhodium exhibits an unusual characteristic. This will be discussed in connection with the thermionic current as a function of temperature. The factors affecting the behavior of rhodium below 240°C are complicated and it

is not always possible to predict in advance the exact type of curve that will result when the temperature is decreased from 240°C to room temperature. The data for the curves in Figs. 3 and 4 were taken under apparently the same conditions, yet the final currents at room temperature are very different. In the case of the curve in Fig. 3—the more frequent type of curve —the final photo-current observed with zero heating current was not stable, but decreased in approximately one hour from the value at *A* to the value at *B*. Under the conditions of Fig. 4 on the other hand a stable condition was reached at once by the same gradual reduction of the heating current to zero. If the heating current was instantly reduced to zero when the filament was at about 1250°C (heating current of 12 amperes) the stable condition represented by *B* would always be reached in about 10 minutes. As mentioned above, almost half of this delay is accounted for by the time required for the filament and its surrounding cylinder to cool to room temperature. The behavior in the range from 240°C down depends also upon the vacuum conditions, a sequence such as that of Fig. 4 occurring only under the best conditions. The complicated situation which these curves suggest will be discussed later.

The Photoelectric Long Wave Limit

During the early stages of outgassing, the long wave limit was obtained by means of Corning glass filters. The final value, however, was located by using various solutions of tartaric acid, acetic acid, and the glass filters. Spectrograms of all filters were made at the same time that they were used. The wave limit was between 2378A and 2482A before any heat treatment. The specimen was heated for five hours at 500°C after which the long wave limit was between 2536A and 2752A. During the baking period of 94 hours it decreased to about 2536A. Then, on heating the rhodium at temperatures

Table I.

Time of heating specimen (hours)	Heating temperature (degrees C)	Long wave limit (angstroms)
25	900	2967
59	1025	2804–2967
81	1025	2804–2967
144	1025	2967–3341
190	1250	2967–3341
213	1250	(2536)–2752
267	1250	(2536)–2752
419	1250	2652–2752
676	1250	2482–2536
1051	1450	2482–2536

varying from 900°C to 1450°C, its long wave limit varied with time of outgassing as indicated in Table I. During the latter 375 hours the long wave limit remained between the 2482A and 2536A lines. Both of these lines are very intense and the limit could be very definitely located between them. If this limit is taken to be characteristic of outgassed rhodium, Einstein's[12] photoelectric equation gives for its photoelectric work function at 25°C

[12] Einstein, Ann. d. Physik **17**, 132 (1905).

$$V = \frac{ch\nu_0}{e} = \frac{c^2h}{e\lambda_0} = \frac{12335}{\lambda_0} = 4.92 \pm 0.06 \text{ volts},$$

where Birge's[13] values for the constants are used and λ_0 is (2482+2536)/2A. The long wave limit for the rhodium at approximately 240°C (corresponding to a heating current of 2.5 amperes) was found to lie between the 2652A and 2752A lines. The average of these values gives for the photoelectric work function at 240°C

$$V = \frac{12335}{2702 \pm 50} = 4.57 \pm 0.09 \text{ volts}.$$

No further change in long wave limit has been observed up to 650°C. Nevertheless, the photo-current continues to increase up to 950°C. An increase in temperature, therefore, appears to increase both the surface work function and the quantum efficiency.

Thermionic Current as a Function of Heating Current

The thermionic current was measured with a Leeds and Northrup galvanometer which had a sensitivity of 1.57×10^{-10} amperes per mm deflection at a scale distance of 1.5 meters. In Fig. 5 the thermionic current is plotted

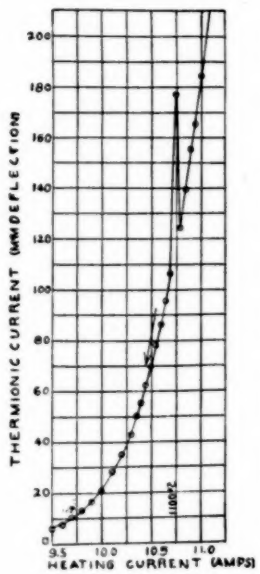

Fig. 5.

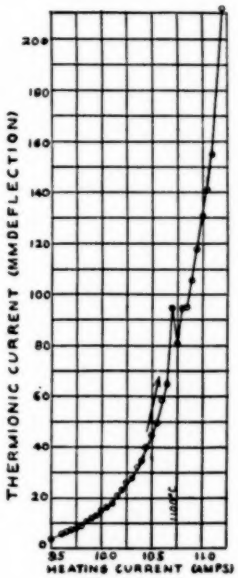

Fig. 6.

as a function of the heating current in amperes. The most interesting part of the curve is at approximately 10.7 amperes (about 1100°C) where the thermionic current is irregular. In the case of gradually decreasing the heating current and observing the thermionic current at short intervals of heating

[13] Birge, Phys. Rev. Supplement **1**, 1 (1929).

current, the writer has been able to obtain at about 10.7 amperes of heating current a gradual increase in the thermionic emission (heating current kept constant) until it reached a maximum value corresponding to an increase of temperature of approximately 25°C and then a gradual decrease in emission until equilibrium was reached at a value very close to what it was before the gradual increase began (see Fig. 6). This phenomenon indicates that at about 1100°C a change which liberates heat takes place on cooling rhodium.

Cardwell[14] published a similar thermionic curve for iron in which the thermionic current was irregular at 910°C, where the crystal structure changes from the body centered cubic to the face centered cubic type. One would think that the similar break in the thermionic curve for rhodium is due to the same cause; that is, to a change in the crystal structure. However, it is possible that the break is due to absorption or evolution of gas at this temperature. Nevertheless, it must be remembered that this specimen of rhodium had had more than 600 hours of heat treatment at about 1250°C in a final vacuum of 10^{-8} mm of Hg when the data for this curve were taken, and also that it has been impossible to detect any change in pressure peculiar

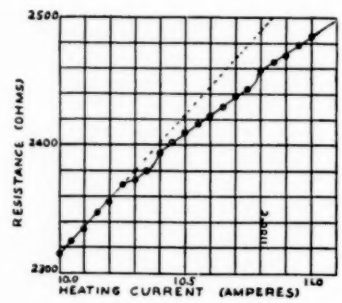

Fig. 7.

to this particular temperature while increasing or decreasing the heating current. The crystal structure of rhodium at various temperatures is now being determined in this laboratory by means of x-rays.

Mendenhall and Ingersoll[15] observed an anomaly at about 1050°C, consisting of an easily reversible change in the radiation of the surface of a small sphere of rhodium heated on a Nernst glower. They reported further that, as the temperature was lowered, the sphere became rather suddenly brighter —the change being seen to spread rapidly over the globule—and that, if the temperature was raised again, the reverse change took place. The fact that these observations were in air at normal pressure, while the present observations were in a very high vacuum, favors the view that the cause is a structure change rather than a gas action.

Resistance as a Function of Heating Current

In Fig. 7 the resistance of the specimen of rhodium is also plotted as a function of the heating current. It is interesting to observe that, at about

[14] Cardwell, Nat. Acad. Sci. **14,** 439 (1928).

[15] Mendenhall and Ingersoll, Phil. Mag. **15,** 205 (1908).

10.3 and 10.7 amperes of heating current, a definite change in slope occurs in the resistance curve. It is reasonable to suppose that the two breaks are due to uneveness of the temperature of the filament, because this curve was taken after the filament had been heated for 575 hours at approximately 1250°C. The fact that the slope of the resistance curve changes abruptly suggests the idea that a change in the structure may be taking place in the rhodium.

The Thermionic Work Function

The black-body temperatures of the rhodium strip were measured with a disappearing filament type of optical pyrometer which had been calibrated at the gold and palladium points and sectored down from the palladium point to the gold point. The readings were corrected for the transmission of the Pyrex window by means of data taken before it was sealed to the experimental tube. Then the true temperatures were computed from the relation

$$1/T - 1/S = \lambda \log \epsilon / c_2 \log e,$$

where T is the true temperature, S the apparent temperature, λ the wavelength used, ϵ the emissivity,[16] c_2 a constant in Wien's equation, and e the

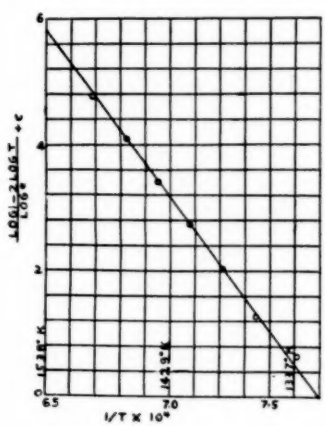

Fig. 8.

Naperian base. Fig. 8 gives the relation between $(\log i - 2 \log T)/(\log e) + C$ and $1/T$. The slope of this curve is the b in Richardson's relation

$$i = AT^2 e^{-b/T},$$

where i is the thermionic current and A is a constant.

$$b = 53{,}100° K.$$

Hence, the thermionic work function is

$$V = \frac{bk}{e} = \frac{53100 \times 1.371 \times 10^{-16} \times 299.8}{4.770 \times 10^{-10}} = 4.58 \text{ volts}.$$

[16] Bulletin of Bureau of Standards **11**, 595 (1914–15).

From other curves it is estimated that the result can be reproduced easily within 2%. Therefore, the thermionic work function is 4.58 ± 0.09 volts. This value agrees with the value given for the photoelectric work function at 2.5 amperes of heating current (approximately 240°C).

The Effect of Pure Hydrogen and Oxygen on Outgassed Rhodium

Extreme care was given to the purification of the hydrogen and oxygen used in this work. Hydrogen, admitted to the experimental tube after 500 hours of heat treatment for the rhodium, changed the long wave limit from the equilibrium value of 2482–2536A (a value characteristic of rhodium after 1000 hours of heat treatment in a final vacuum of 10^{-8} mm of Hg) to 2378–2482A; that is, the limit was changed to approximately the original value characteristic of the specimen before it had received any heat treatment. The photo-current was decreased very quickly from 100 mm deflection to 2 mm. Heating the specimen at 1000°C for one minute in hydrogen at a pressure of one mm of Hg increased the photo-current from 2 mm to 100 mm deflection, but the photo-sensitivity dropped to 3 or 4 mm in 4 minutes after reducing the heating current to zero. Allowing the pumps to remove as much of the hydrogen as possible without heating the rhodium increased the photo-current from 2 mm to 4 mm. Light from the mercury arc increased the photo-current from 2 mm to 4 mm in two hours. The long wave limit characteristic of the rhodium after 1000 hours of heat treatment was attained in 100 hours of heating at 1250°C after this exposure to hydrogen. It is evident that rhodium occludes and adsorbs hydrogen quite well since its photoelectric properties are radically affected by the presence of hydrogen.

Oxygen, admitted to the system after the specimen had regained its stable condition after the introduction of hydrogen, changed the long wave limit from its equilibrium value of 2482–2536A to a value below 2300A. Oxygen was more effective in decreasing the long wave limit than hydrogen. Heating the specimen at 1000°C for one minute in oxygen at a pressure of 1 mm of Hg did not restore the photo-current to its original 100 mm deflection. In order to attain stable conditions again it was necessary to heat the specimen at 1250°C for 100 hours and to heat by means of a torch the high vacuum end of the system several times during this interval.

The following peculiarities of the photoelectric behavior below 240°C require further consideration:

(1) The stable value of the work function at room temperature is 4.92 volts; at 240°C this has changed to 4.57 volts, but no further change is observed from there on up to 650°C.

(2) When the rhodium was cooled as rapidly as possible from 1250°C to room temperature, the stable condition would be reached in 10 minutes after stopping the heating current.

(3) When the temperature was varied slowly from above 240°C, the more usual form of ascending and descending photo-current curve is shown in Fig. 3. Condition *A* is not stable, but changes to *B* in the course of an hour.

(4) Under the best attained vacuum conditions (10^{-8} mm of Hg) a different cycle is observed (Fig. 4) and with the same rate of change of temperature as in Fig. 3, the stable condition (*B*) is reached at once.

(5) It is to be noticed that the better the vacuum (Fig. 4) the more sudden are the changes in photo-current with temperature.

The question is, are these peculiarities caused by changing surface contamination, or do they indicate a structure change in the rhodium occurring at or below 240°C? A simple calculation shows that with a pressure of 10^{-8} mm of Hg and assuming no molecular reflection, it would take from one-half to several hours to form a monomolecular layer on the metal, according to the density one assumes for the gas layer. Hence from (2) above it does not seem likely that condition *B* is due to a gas covered surface, unless the gas layer is stable at high temperatures (1250°C) as well as at room temperature, being perhaps a hydride. Furthermore, in order to account for (1) and (3) this gas layer or hydride must be assumed to be unstable from 240°C up to some higher temperature, the relatively rapid rise in the ascending curve of Fig. 3 being due to the breaking up of the layer. But this does not fit (5), for the sudden drop in the descending branch of Fig. 4 would have to be attributed to the partial formation of the layer, and such rapid formation would be *less* likely to occur under the extremely high vacuum conditions of Fig. 4 than under the somewhat lower vacuum conditions of Fig. 3—which is contrary to fact. The sudden changes so prominent in Fig. 4 strongly suggest that there is an allotropic change at 240°C, and that the structure stable above this temperature can be carried down to lower temperatures in an irregular way, depending upon circumstances. A comparison of Figs. 3 and 4 suggests furthermore that the influence of this change in structure can be easily obscured by changing contamination except under the very best vacuum conditions. This is, however, not a completely satisfactory interpretation of the results.

In conclusion, the writer wishes to express his sincere thanks to Dr. C. E. Mendenhall, under whose direction this work has been done, to Mr. J. B. Davis, the glass-blower, and to Mr. J. P. Foerst, the mechanician.

THE EFFECT OF RESOLVING POWER ON MEASUREMENTS OF THE ABSORPTION COEFFICIENT OF ELECTRONS IN GASES

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(Received November 26, 1930)

Abstract

The absorption coefficient of electrons has been studied as a function of the resolving power of the experimental apparatus. An electron beam of 0.4 mm radius was used in a Mayer type of apparatus in which the opening at the end of the scattering chamber was of variable aperture. Values of the absorption coefficient were obtained in helium and in mercury vapor for 20, 40, 80 and 135 volt electrons over an angular aperture range of from 2° to 11° as measured from the end of the electron gun. All curves showed a definite decrease in the absorption coefficient with increase in angular aperture. These curves were corrected for the positive ion current, from the efficiency of ionization data of Bleakney and Smith, to give curves for the total number of electrons collected as a function of the size of the opening. These showed also a definite decrease with increase in aperture, corresponding to a preference for scattered electrons to be deflected through small angles. In helium the curves were steeper the higher the electron velocity, indicating that this preference is more decided for fast electrons than for slower electrons. In mercury vapor the curves were more nearly alike. The results do not indicate as decided a preference for small angle scattering as is indicated by the angular distribution curves of Arnot in mercury vapor. This discrepancy is not explained.

Introduction

EXPERIMENTS [1,2,3,4] designed to determine the angular distribution of electrons after collision with gas molecules indicate a decided preference for small angle scattering. In fact, most of the published curves show a a continued increase in the probability of scattering with decrease in angle, down to as small angles as have been obtained. Such curves for slow incident electrons are not so steep, in general, as are those for faster electrons, but in all cases the scattered electrons show this definite tendency to be concentrated about the forward direction.

The term "absorption coefficient" as applied to electron scattering by gas molecules has concerned itself with a determination of α from the relation $I = I_0 e^{-\alpha x p}$. In such experiments electrons of a definite velocity are caused to move in a beam (whose size and shape depend on the defining electrode system) through a scattering chamber of length x which contains a gas at a known pressure, p. On passing through this scattering chamber certain

[1] E. G. Dymond and E. E. Watson, Proc. Roy. Soc. **A122,** 571 (1929).
[2] G. P. Harnwell, Phys. Rev. **33,** 559; **34,** 661 (1929).
[3] F. L. Arnot, Proc. Roy. Soc. **A125,** 660 (1929).
[4] J. H. McMillen, Phys. Rev. **36,** 1034 (1930).

encounters with gas molecules cause some of the electrons to leave the beam, and so the beam of initial current strength, I_0, is reduced to the value I as given above. Experimentally two general methods have been used to determine α. The path of the electron beam may be a straight one as in a Mayer[5] type of apparatus, or the beam may be focused over a semicircular path by means of a magnetic field as was first done by Ramsauer.[6]

If $I'=I_0-I$ is the current to the scattering chamber, then, for low pressures, from the exponential relation given above, α is proportional to I'/I_0. Thus a determination of α for a particular apparatus is equivalent to measuring the fractional current to the scattering chamber. For low velocity electrons this current is composed merely of those electrons which have been deflected through an angle greater than some average minimum angle, $\bar{\theta}$. This angle is a function of the size of the opening at the end of the scattering chamber and of the length of the path. For electrons with a velocity greater than a certain value there may be ionization at an encounter which will result in at least three charged particles. A certain fraction of these will be collected, depending on the apparatus. If $\Phi_s(\theta)$, $\Phi_e(\theta)$ and $\Phi_i(\theta)$ are the probabilities that the initial electron, the ejected electron and the ion, respectively, will move in the direction θ after such an encounter, and if F^+ is the probability of ionization taking place, then for a Mayer type of apparatus the fractional current to the scattering chamber is

$$I'/I_0 = \int_{\bar{\theta}}^{\pi} (\Phi_s + F^+\Phi_e + F^+\Phi_i)d\theta \qquad (1)$$

where the integral is taken over the possible angles of collection. If it is assumed that the ion has an equal probability of moving in any direction, Φ_i is a constant and the integral of the third term does not change much with a small change in the lower limit of integration, $\bar{\theta}$. The second term, representing the angular distribution function for the ejected electrons has not, to the author's knowledge, been investigated. This distribution may be uniform but it seems more probable that it would be somewhat similar to the distribution for the scattered primary electrons. The first term in the integrand is the probability function, $F(\theta)$, which is measured in angular scattering experiments. As has already been mentioned this function is one which in general increases with decreasing θ, being of particular weight for values of θ near $\bar{\theta}$. Hence one would expect that a small change in the lower limit of integration would produce a large change in the value of Eq. (1). Any distribution of the ejected electrons other than a uniform distribution would enhance this effect. Thus the current collected by the scattering chamber is very decidedly a function of the resolving power of the apparatus. In the Ramsauer type of apparatus the integrals of the second and third terms of Eq. (1) will probably just balance each other. Both the ejected electron and ion will have such energies that their paths will have a smaller radius of curvature than that of

[5] H. F. Mayer, Ann. d. Phys. **64**, 451 (1921).
[6] C. Ramsauer, Ann. d. Phys. **66**, 547 (1921).

the main electron beam, and hence even if initially they were directed along the electron beam they would soon leave it and balance each other at the walls of the scattering chamber. At such an encounter, or any encounter in which the initial electron loses an appreciable amount of energy it too will be removed from the beam regardless of its direction of motion immediately following the encounter. Thus a Ramsauer type of apparatus measures not only the integral of the first term of Eq. (1) but also an additional negative current due to those electrons which lose energy even though they are deflected through angles less than $\bar{\theta}$. On the other hand, in a Mayer type of apparatus the integral of the first term is partially balanced by a part of the positive ion current.

From these considerations one would expect that the magnitude of the absorption coefficient as obtained by various observers using apparatus with different resolutions should exhibit quite a wide range of values. But this does not seem to be the case. Recent measurements by Maxwell,[7] Jones[8] and Brode[9] on the absorption coefficient for electrons in mercury vapor agree much better than would be expected. The author* has also carried out a determination with a Mayer type of apparatus (separate from that used for the work reported in this paper) in which electrons scattered through angles down to 3°, on the average, were counted as having collided. The absorption coefficient was determined for electrons of from 5 to 100 volts velocity and the values agreed within a few percent with those obtained by Brode with a Ramsauer apparatus. These values are but 25 percent greater than those reported by Maxwell. His apparatus defined a collision only if it resulted in a very much larger deflection of the electron. Arnot[3] has obtained an angular scattering curve for electrons in mercury vapor, and a numerical integration of this curve as applied to each individual apparatus indicates that there should be a much greater divergence in the results. Similarly for other gases various observers obtain results more in accord with each other than would be expected.

It was then decided to build a Mayer type of apparatus in which the opening at the end of the scattering chamber could be changed in size, so that the absorption coefficient could be studied in one particular apparatus as a function of the resolving power. Such a study should throw light on the probability of angular scattering, and should enable a check of existing curves Recently Metta Clare Green[10] carried out a similar investigation, but found no consistent variation of the absorption coefficient with opening. Inasmuch as such a result is so definitely in opposition to the results of angular distribution experiments and as the magnitudes of the values obtained for the absorption coefficient differed, in most cases, so radically from accepted values,

[7] L. R. Maxwell, Proc. Nat. Acad. Sci. **12,** 509 (1926).
[8] T. J. Jones, Phys. Rev. **32,** 459 (1928).
[9] R. B. Brode, Proc. Roy. Soc. **A125,** 134 (1929).
* Work not published.
[10] Metta Clare Green, Phys. Rev. **36,** 239 (1930).

such a study should still be fruitful. Measurements were accordingly made in helium and in mercury vapor.

Apparatus

The apparatus used is shown diagrammatically in Fig. 1. It was constructed of copper. Electrons from the tip of the filament, F, were accelerated to a definite velocity between the plates D_1 and D_2, and made to travel in a beam of small cross-section through the scattering chamber, sc, and into the Farady cage, FC. The diameters of the circular openings in the gun, G, were 0.75, 0.50, 0.50 and 0.75 mm for D_1, D_2, D_3 and D_4 respectively. D_5 was about 1.5 mm in diameter, and less than 1 mm from D_4. The distance from D_1 to D_2 was 5.0 mm and from D_1 to the end of the gun, D_4, was 45 mm. The scattering chamber, from D_4 to D_6, was 4.0 cm in length, and the Faraday cage was 16 cm in length. The hairpin filament was a small tungsten wire bent sharply at the opening D_1. It required about 1.5 amperes for satisfactory electron emission. All diaphragms were slightly bevelled, and important surfaces were given a light coat of soot.

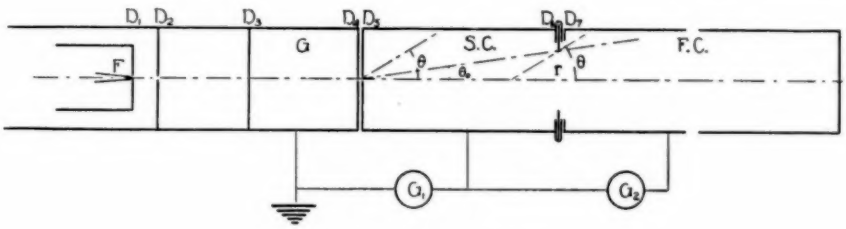

Fig. 1. Diagram of apparatus.

The variable aperture at D_6 was obtained by the use of a 30 cm strip in which were cut a series of holes of different size. The strip could be slid freely back and forth by means of a special magnetic control, which was constructed such that all magnetic material could readily be removed for each reading.

The apparatus was sealed in a Pyrex tube free from wax joints, and vacuum conditions were such that a pressure of less than 10^{-6} mm mercury would build up in 24 hours when the tube was cut off from the pumps. For the measurements in mercury vapor, a trap containing mercury was maintained at a definite temperature, and the calculations were based on the vapor pressure corresponding to that temperature as recorded in the International Critical Tables. Pressures corresponding to various temperatures up to about 20°C were used. The gas pressures for helium were determined from McLeod gauge readings. A side tube containing carbon which had been baked out for several hours at 500°C was used in conjunction with the helium measurements. This tube and the mercury trap were kept at the temperature of liquid air.

A pair of large Helmholtz coils was used to neutralize the earth's field, and the tube was mounted such that the electron beam traveled along the axis of the coils.

METHOD

In a determination of α from the exponential decrease in the intensity of an electron beam a constant, K, must be introduced to account for those electrons which would be collected by the scattering chamber regardless of gas pressure. This constant should depend only on the geometry of the apparatus. The beam of initial strength I_0 is then reduced to $I = KI_0 e^{-\alpha x p}$ after traveling a distance x in a gas at pressure p. The current ratio I/I_0 was measured by the galvanometers, G_2 and G_1 (Fig. 1) for different gas pressures and for different openings at the end of the scattering chamber. From the above equation

$$\log I/I_0 = \log K - \alpha x p/2.3 \tag{2}$$

in which the logarithms are taken to the base 10. If K is a constant, independent of the pressure and electron current for a particular resolution, the log I/I_0 should exhibit linearity when plotted against the pressure. The

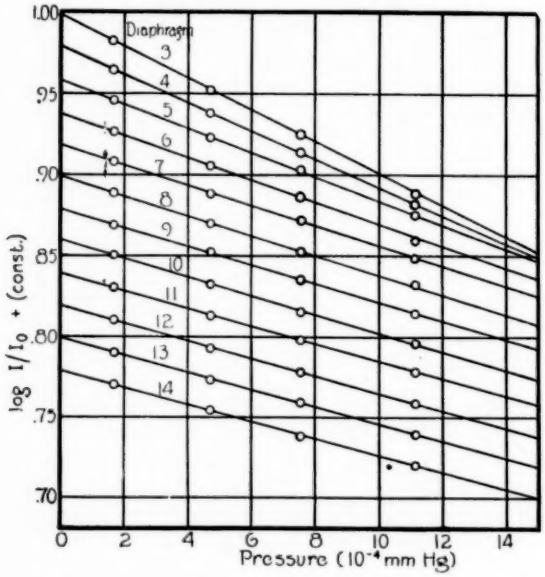

Fig. 2. To show linearity between log I/I_0 and pressure. (80 volt electrons in mercury vapor.)

slope of such a straight line relationship being $\alpha x/2.3$ makes it possible to calculate α. If the pressure used is the observed pressure corrected for thermal diffusion and reduced to the corresponding pressure at 0°C, α is obtained in the usual units, cm^2/cm^3 per mm pressure at 0°C.

Fig. 2 shows the relation between log I/I_0 (plus an arbitrary constant) and the pressure for 80 volt electrons in mercury vapor; each curve was obtained with a different opening at the end of the scattering chamber. These curves indicate that K was independent of the pressure in each case. The value of log K = log I/I_0 when $p=0$ shows that K was greater than 0.99 for all openings. Thus at least 99 percent of the original beam was collected by

the Faraday cage when no gas was present. This means that the number of secondary electrons reflected into the scattering chamber from the end of the gun or the end of the Faraday cage was at a satisfactory minimum.

By applying a retarding field between the Faraday cage and the scattering chamber (Fig. 1) the velocity distribution of the electron beam was found to be quite satisfactory. For a 40 volt electron beam, over 95 percent of the electrons had velocities within a few tenths of a volt of the mean. Though this differed from 40 volts by a small amount, the beam will nevertheless be designated as a 40 volt electron beam. The correction will also be disregarded for the other velocities used.

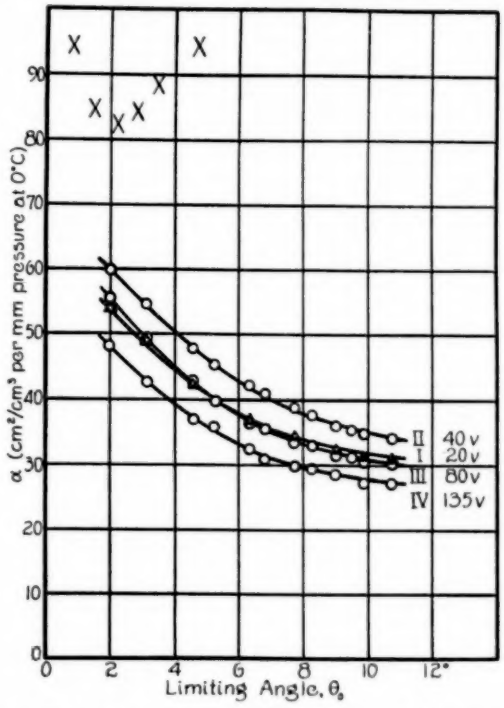

Fig. 3. "Absorption coefficient," α, as a function of the resolving power of the apparatus, in mercury vapor. (X-values given by Metta Clare Green for 37.5 volt electrons.)

The values of α in mercury vapor were for the most part obtained from such curves as those in Fig. 2, which in turn had been determined by four different pressures. Those for helium and some of the mercury values were obtained with but two pressures, one of which was usually zero. The path length value of $x = 4.0$ cm was used for all the calculations.

Results and Discussion

The results of the measurements in mercury vapor are given graphically in Fig. 3, and those for helium in Fig. 4. α is plotted for 20, 40, 80 and 135 volt electrons against the limiting angle, θ_0, giving curves I, II, III and IV respectively. Referring to Fig. 1, this limiting angle is defined as $\theta_0 = \tan^{-1} r/l$

where r is the radius of the opening and l is the length of the scattering chamber. If any electron is deflected through an angle less than this it will not be counted as having collided. The range of values for θ_0 corresponds to a range of diaphragm radii of from 1.4 to 7.6 mm. The experimental points for mercury are averages of two complete sets of readings, differing from each other in most cases by less than 2 percent. The values for helium are averages of

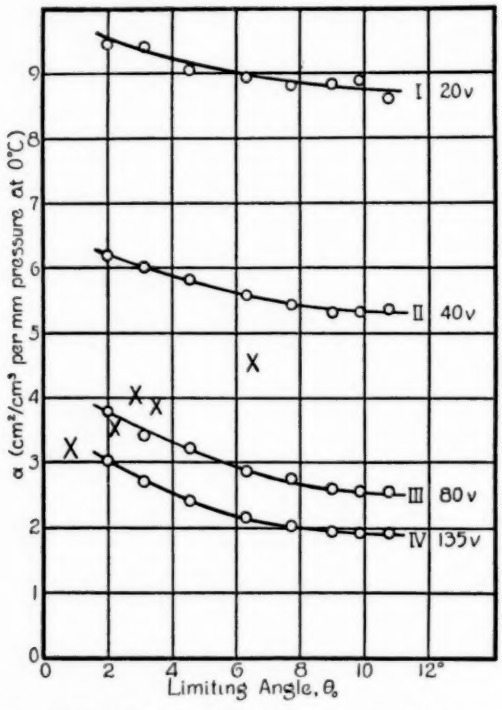

Fig. 4. "Absorption coefficient," α, as a function of the resolving power of the apparatus, in helium. (X-values given by Metta Clare Green for 97 volt electrons.)

four sets of readings with a somewhat larger experimental error. All of the curves show a definite decrease in the absorption coefficient as the size of the opening increases. This, of course, corresponds qualitatively to the tendency for scattering to take place in the forward direction.

If $K=1$, which has been seen to be practically the case, the current to the scattering chamber is $I'=I_0-I=I_0(1-e^{-\alpha x p})$. For low pressures this becomes

$$I'/I_0 = \alpha x p \tag{3}$$

or, α is numerically equal to the negative current to the scattering chamber in terms of a certain number of electrons per primary electron per cm path per mm pressure at 0°C. Thus the curves of Figs. 3 and 4 give the relative negative current collected by the scattering chamber when the size of the opening is changed. As has already been seen, this negative current is the resultant of a positive ion current combined with the scattered and ejected

electron current, the fraction which is due to positive ions depending on the probability of ionization. Hence if these curves are to be discussed with regard to the characteristics of electron scattering they must be corrected for the positive ion current. This correction is made possible by the recent work of Bleakney[11] and of Smith[12] who have determined the efficiency of ionization of electrons in various gases. If F^+ is this efficiency of ionization

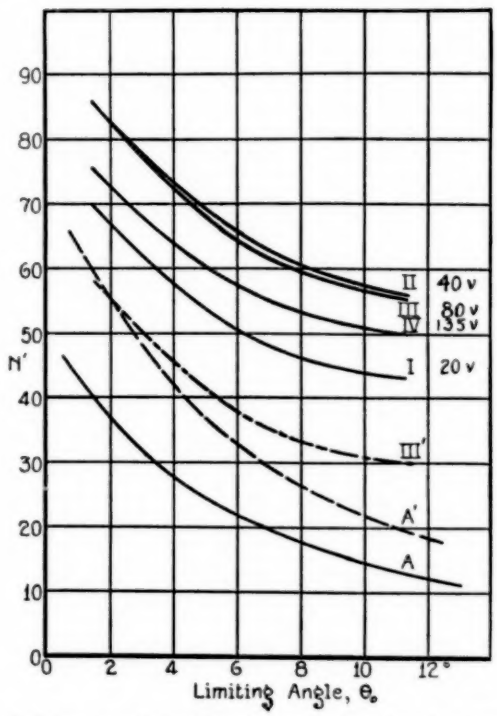

Fig. 5. Number of electrons collected by the scattering chamber, per cm path per primary electron per mm pressure at 0°C, as a function of the resolving power, in mercury vapor. (Curve *A* predicted, as the number of primary electrons scattered, by Arnot's results for 80 volt electrons.)

(given in terms of the number of units of positive charge formed per cm path per primary electron per mm pressure at 0°C) and we assume that the ion has an equal probability of going in any direction,* the positive current to the scattering chamber can be obtained by a simple integration. It is of course a function of θ_0 and is found to vary from $1.10F^+$ at $\theta_0=2°$ to $1.03F^+$ at

[11] Walker Bleakney, Phys. Rev. **35**, 139 (1930).

[12] P. T. Smith, Phys. Rev. **36**, 1293 (1930).

* This assumption seems valid providing the interior of the scattering chamber is a field-free space. A recent investigation by Arnot (Proc. Roy. Soc. **A129**, 361 (1930)) indicated that the positive ions tend to move out perpendicularly to the electron beam. It is doubtful whether his results may be applied here, for they were obtained under different conditions. Intense electron beam currents up to 25 micro-amperes were used, whereas in the work reported here this current did not exceed a tenth of a micro-ampere. However, the results to follow would be substantially the same, even though we accepted Arnot's distribution for the positive ions.

$\theta_0 = 10°$. The values of F^+ given by Bleakney for 20, 40, 80 and 135 volt electrons in mercury vapor are 12.0, 21.2, 25.0 and 22.5 respectively; those given by Smith for the respective voltages in helium are 0.00, 0.63, 1.18 and 1.24. With these values the corrections can be calculated and applied to the curves of Figs. 3 and 4. The corrected curves, representing the total number of electrons collected by the scattering chamber (per primary electron per cm path per mm pressure at 0°C), are given in Figs. 5 and 6, for mercury vapor and helium, respectively. Since these curves deal only with the electrons which are collected they may be used in a comparison of electron scattering.

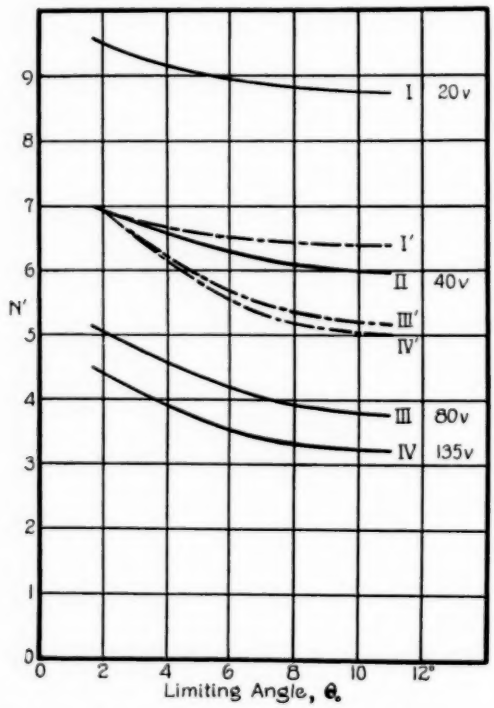

Fig. 6. Number of electrons collected by the scattering chamber, per cm path per primary electron per mm pressure at 0°C, as a function of the resolving power, in helium.

To get a better idea of the relative dependence of this scattering on angular aperture for the different primary velocities, the 20, 80 and 135 volt curves in helium (Fig. 6) have been multiplied by the proper factors to make them coincide with the 40 volt curve at $\theta_0 = 2°$, giving the new curves I′, III′ and IV′ respectively. From this set of curves we notice that as the velocity of the primary electrons becomes greater, the curves become relatively steeper; i.e., a small change in the size of the opening cuts out a relatively greater number of the scattered electrons if the primary electrons have high velocity than if they have a lower velocity. This indicates that scattering of fast electrons is more definitely concentrated in the forward direction than that for slow electrons, and corresponds to the decrease in steepness

of the angular scattering curves with decrease in primary electron velocity, as observed by McMillen.[4] Mercury vapor however, does not exhibit such a marked relative preference. The curves in Fig. 5 show about the same relative change over the range of angles used, being much more alike than are those in helium. This indicates that the angular distribution of scattered electrons in mercury vapor is quite similar over the velocity range of from 20 to 135 volts. This does not imply, however, that the angular distribution for the scattering of primary electrons would be the same over this velocity range. To say anything about this, the distribution of the ejected electrons must be taken into consideration, and it is not likely that this distribution would be the same for primary electrons of different velocities. These relations cannot be checked with existing data for, aside from our lack of knowledge of the behavior of the ejected electron, no investigation has as yet be published in which the angular distribution has been studied as function of electron velocity in mercury vapor.

From the angular scattering curves of Arnot for 80 volt electrons in mercury vapor it is possible to predict the number of primary electrons which should be collected by the scattering chamber for any size opening. He determined the angular distribution for electrons which had not lost energy and also for those which had lost energy. He assumed that these electrons were all primary electrons, even though there is the possibility that an ejected electron may be given sufficient energy such that it will be confused with the group of primary electrons which had lost energy. The calculation for the number of primary electrons collected according to his results can be done in the following way.

Let $F(\theta)d\theta$ be the number of electrons scattered between θ and $\theta+d\theta$ per primary electron per cm path at a definite temperature and pressure. The effective length of path over which electrons deflected through angle θ are collected is $l_e=l-r/\tan\theta$, as can be seen from Fig. 1. Then for N_0 primary electrons the number of electrons deflected between θ and $\theta+d\theta$ which are collected by the scattering chamber is $N_0pF(\theta)l_ed\theta$ for a gas pressure p which is sufficiently small. The total number collected will then be

$$N' = N_0p\int_{\theta_0}^{\pi}F(\theta)(l-r/\tan\theta)d\theta. \tag{5}$$

It may be noted that this includes all electrons scattered into the chamber, even those which are deflected through angles greater than 90° giving for them the proper effective path length which is greater than 1. If $F(\theta)$ be known, the function $F(\theta)$ $(l-r/\tan\theta)$ can be plotted against θ for different values of r, and the areas under the resulting curves will represent the relative numbers of primary electrons collected by the scattering chamber for openings of different size. The only assumption which has been made is that the scattering takes place along the axis of the apparatus.

Compton[13] has tabulated Arnot's values for the scattering of 80 volt

[13] K. T. Compton, Rev. Mod. Phys. **2**, 123 (1930).

electrons in mercury vapor in terms of the number of electrons scattered per unit solid angle at angle θ per primary electron per cm path at 20°C and 0.001 mm pressure. $F(\theta)$ is then this function multiplied by $2\pi \sin \theta$. By using these values for $F(\theta)$ and performing the numerical integrations outlined above, $N'/N_0 p$ was obtained for different values of the diaphragm radius. On correcting this result to 0°C and 1 mm pressure (since $F(\theta)$ was given for a temperature of 20°C and a pressure of 0.001 mm) and dividing by the path length, $x = 4.0$ cm, one obtains the predicted values for the number of primary electrons which should be collected by the scattering chamber for various apertures. Curve *A* of Fig. 5 is the result of this work, plotted in terms of $\theta_0 = \tan^{-1} r/l$. Curve III of the same figure represents the actual number of electrons which were collected experimentally. Assuming the validity of both curves, the difference between their ordinates for a particular value of θ_0 would represent the number of ejected electrons collected by the scattering chamber for that value of θ_0. This difference increases with increasing θ_0 which means that a larger ejected electron current would be collected the larger the diaphragm opening. Such a result can be interpreted only if the ejected electrons obey a distribution which favors scattering in the backward direction, which does not seem reasonable. It is of interest to compare the curves if we assume a uniform distribution for the ejected electrons. The correction to be made to curve III will be practically the same as (but opposite to) the correction which was made for the positive ions, and the resulting curve will be similar to the curve for α. This is given in Fig. 5 as curve III′. To compare this curve with Arnot's the latter has been plotted to a different scale giving curve *A*′. Both curves, of course, show the preference for small angle scattering, but Arnot's curve makes this preference much more decided. If we had assumed an angular scattering for the ejected electrons favoring scattering in the forward direction, curve III′ would have differed much more decidedly from Arnot's predicted curve. It is to be mentioned that Arnot's results were obtained with primary electron currents of several micro-amperes, whereas in the present work no currents greater than a tenth of a micro-ampere were used. As was noted above, the only assumption made in the calculation was that the scattering should take place along the axis. This was approximated quite well, for tests at the end of the scattering chamber indicated that the beam was but 0.8 mm in diameter and hence all of the scattering took place within 0.4 mm of the axis. Thus there remains a definite discrepancy between the two curves which is difficult to explain.

It is of interest to note that the procedure we have just outlined may be reversed, and $F(\theta)$ may be obtained from the experimental curve. Thus, if the experimental curve gives the result

$$f(\theta_0) = \int_{\theta_0 = \tan^{-1} r/l}^{\pi} F(\theta) \cdot (l - r/\tan \theta) d\theta \tag{6}$$

then $F(\theta)$ can be determined by differentiating this equation twice. This gives

$$F(\theta_0) = \sin\theta_0/l\left(\cos\theta_0\frac{d^2f(\theta_0)}{d\theta_0^2} - 2\sin\theta_0\frac{df(\theta_0)}{d\theta_0}\right). \quad (7)$$

This equation, however, is rather impractical of application for the second derivative bears too much weight. A small error in the experimental determination of $f(\theta_0)$ is amplified in the calculation, which makes $F(\theta)$ very uncertain.

The results of Metta Clare Green[10] which were previously mentioned are given by the crosses in Figs. 3 and 4, for certain electron velocities in mercury vapor and helium. These values are also plotted in terms of $\theta_0 = \tan^{-1}r/l$ where $l = 7.5$ cm in her apparatus. For a given electron velocity she found no definite variation in the absorption coefficient with change in aperture, all the values for a given curve lying within the experimental error of the mean of that group. However such a result is in direct opposition to all angular scattering experiments. In addition, the magnitudes of the values obtained for the absorption coefficient differed in most cases so radically from those obtained by any other observer that it is difficult to place much weight on the results. This may, in part, have been caused by the penetration of electric fields into the scattering chamber at both ends. Such experiments necessitate that the scattering be studied in a field-free space. Otherwise it is difficult to determine the cause of this discrepancy.

This investigation has given further evidence that when electrons are scattered by gas molecules they exhibit a preference for deflection through small angles. It has also been shown that, over the velocity range studied, fast electrons show a greater relative tendency to be deflected through small angles than do slower electrons. This is quite definitely the case for scattering in helium, whereas it is not so marked in mercury vapor. Further, the results in mercury vapor do not indicate as decided a preference for forward scattering as do those of Arnot.

The author wishes to express his gratitude to Professor Tate for his many helpful suggestions and continued interest throughout this work.

HIGH FREQUENCY DISCHARGES IN MERCURY, HELIUM AND NEON*

By Charles J. Brasefield
University of Michigan

(Received November 15, 1930)

Abstract

Measurements were made of the potential drop at the electrodes and the electric force in the positive column of high frequency discharges in mercury, helium and neon for a large number of gas pressures and for frequencies of oscillation between 1.25 and 22.5 megacycles. The results showed that in general, the magnitude of the electric force was too small to produce electrons whose velocity would be sufficient to ionize or excite the gas. It was observed that as the frequency of oscillation increases, the potential drop at the electrodes decreases. Considering the total voltage between electrodes it was found that the high frequency discharge in mercury has its maximum conductivity when operated at a frequency of 17.5 megacycles (17.15 meters) and at a pressure of 0.002 mm; the discharge in helium has its maximum conductivity at 17.5 megacycles and 0.33 mm pressure; the discharge in neon has its maximum conductivity at 7.5 megacycles (40 meters) and 1.0 mm pressure.

Introduction

PREVIOUS work[1] on the conductivity of a high frequency discharge in hydrogen showed that a knowledge of the variation of the total voltage across the discharge with the gas pressure and the frequency of oscillation is not sufficient to determine the mechanism of the discharge, for the potential difference between electrodes consists of two parts. The first is the drop in potential in the body of gas. The second is the drop in potential at the electrodes which includes the dielectric loss in the glass under the electrodes and the drop in potential at the electrodes due to the accumulation of positive space charge, if any. In order to compare experimental results with any theory of the mechanism of the discharge, it is necessary to study the electric field in the positive column of the discharge, in particular, its variation with gas pressure and frequency of oscillation.

The apparatus used and the experimental procedure followed were essentially the same as in the work on hydrogen. Measurements were made of the voltage between electrodes necessary to produce a current of 100 milliamperes in the gas, the distance between electrodes being varied from 40 to 100 cm in 10 cm steps. If the values of the total voltage between electrodes are plotted against the corresponding distances between electrodes, a curve is obtained which, in general, approximates a straight line. Assuming that as the distance between electrodes increases, the drop in potential at the electrodes remains constant, then the slope of the line gives the electric field in

* Publication of the Research Organization of the Grigsby-Grunow Company, Chicago, Illinois.

[1] C. J. Brasefield, Phys. Rev. 35, 1073 (1930).

the positive column which when multiplied by $2^{1/2}$ gives the amplitude of the electric force. Extrapolating the curve to zero distance between electrodes, the potential drop at the electrodes is found. Values of the electric force in the positive column of the discharge as well as the potential drop at the electrodes were in this way obtained for a large number of gas pressures and for ten frequencies of oscillation between 1.25 and 22.5 megacycles.

Results

1. Experiments on mercury. The discharge tube used was 120 cm long, 5.2 cm internal diameter while the electrodes surrounding it were of sheet copper 5 cm wide. Except for a mercury reservoir at one end, the whole tube was surrounded by an electric furnace which kept it at a temperature of about 150°C. To regulate the vapor pressure of the mercury, the reservoir

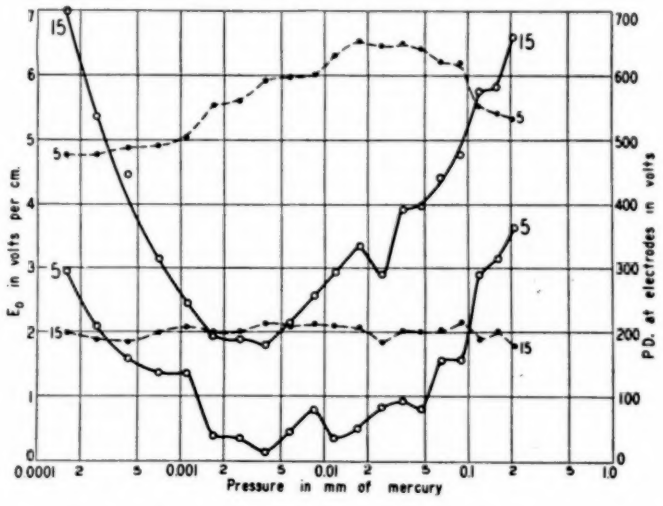

Fig. 1. The variation with pressure of the electric force (solid curves) and the potential drop at electrodes (broken curves) in a high frequency discharge in mercury operated at 5 and 15 megacycles.

was immersed in a water bath which was kept at a constant temperature within 0.2°C during a given run. Measurements were taken at 5° intervals from 0° to 95°C.

Fig. 1 shows, for two typical frequencies of oscillation, the variation with pressure of the electric force and the potential drop at electrodes when a current of 100 milliamperes is passing through the tube. It was observed that as the frequency of oscillation increases, the potential drop at the electrodes decreases from approximately 800 volts at 1.25 megacycles to 200 volts at 15 megacycles. This, without doubt, accounts for the fact that the spark spectrum of mercury was quite pronounced in the region under the electrodes when the discharge was operated at frequencies below 5 megacycles. Considering the total voltage between electrodes, it was found that the discharge

has its maximum conductivity when operated at a frequency of 17.5 megacycles (17.15 meters) and at a pressure of 0.002 mm (25°–30°C).

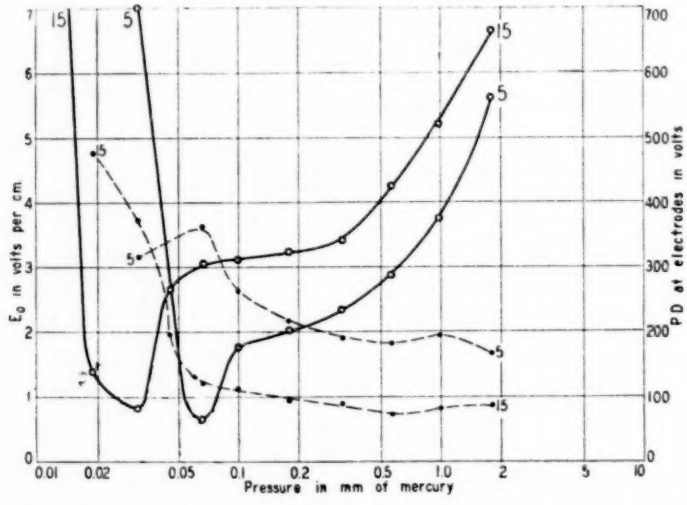

Fig. 2. The variation with pressure of the electric force (solid curves) and the potential drop at electrodes (broken curves) in a high frequency discharge in helium operated at 5 and 15 megacycles.

2. Experiments on helium and neon. The discharge tube used was 130 cm long, 5.1 cm internal diameter while the electrodes surrounding it were of sheet copper 5 cm wide. The helium was purified in a misch metal arc and

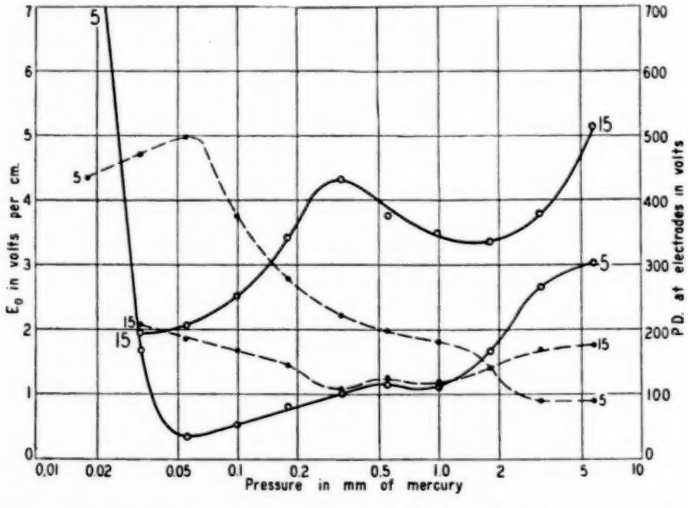

Fig. 3. The variation with pressure of the electric force (solid curves) and the potential drop at electrodes (broken curves) in a high frequency discharge in neon operated at 5 and 15 megacycles.

then circulated over charcoal in liquid air. Spectroscopically pure neon was purchased and further purified by circulation over charcoal in liquid air.

Figs. 2 and 3 show, for two typical frequencies of oscillation, the variation with pressure of the electric force and the potential drop at the electrodes for high frequency discharges in helium and neon carrying 100 milliamperes. As in mercury, the potential drop at the electrodes decreases as the frequency of oscillation increases. Considering the total voltage between electrodes, it was found that the discharge in helium has its maximum conductivity when operated at a frequency of 17.5 megacycles (17.15 meters) and at a pressure of 0.33 mm. The discharge in neon has its maximum conductivity at 7.5 megacycles (40 meters) and 1.0 mm pressure; under these conditions it was possible to obtain a current of 520 milliamperes through the discharge, which was limited, of course, only by the output of the high frequency generator.

In neon, striations were observed at frequencies below 10 megacycles. At frequencies below 5 megacycles, if the pressure was in the neighborhood of 1.0 mm, these striations moved along the tube from one electrode to the other. Moreover, both the direction and velocity of motion could be changed either by varying the current through the tube or, if the current was properly adjusted, by moving one's hand toward or away from the tube. It is suggested that this phenomenon might be produced by beats between plasma ion oscillations and the applied high frequency oscillations.

Discussion

The motion of an electron in a high frequency electric field can be represented by the equation

$$m\ddot{x} = eE_0 \sin(2\pi ft + \delta) \tag{1}$$

where E_0 is the amplitude of the electric force, f the frequency of oscillation and δ a phase constant which depends on the value of E_0 at the instant the velocity of the electron is zero. Integrating Eq. (1), we get the velocity of the electron at any time t,

$$\dot{x} = -\frac{e}{m}\frac{E_0}{2\pi f}\cos(2\pi ft + \delta) + \frac{e}{m}\frac{E_0}{2\pi f}\cos\delta \qquad (v_0 = 0). \tag{2}$$

It is evident that for a given E_0, f and δ, an electron will have its maximum velocity after a time $t = 1/2f$, that is, after it has been under the influence of the electric force for one half cycle. The value of this velocity is

$$v = \frac{e}{m}\frac{E_0}{\pi f}\cos\delta. \tag{3}$$

Moreover, those electrons for which $\delta = 0$ will have the greatest velocity for a given E_0, namely

$$v_{max} = \frac{e}{m}\frac{E_0}{\pi f}. \tag{4}$$

Hence if we substitute for v_{max} the ionizing velocity of electrons for the gas in question, we should get the minimum value of E_0 necessary to sustain a high frequency discharge in that gas. For 10 volt electrons (mercury)

we find $E_{0\min}=0.34\times10^{-6}\times f$ volts per cm. For 25 volt electrons (helium and neon) we find $E_{0\min}=0.53\times10^{-6}\times f$ volts per cm. A glance at Figs. 1, 2, and 3 shows that the majority of the experimental values of E_0 are still less than these minimum values. It appears, therefore, that in the high frequency discharge, electrons whose velocity is sufficient to ionize (or even excite) a gas molecule cannot be produced in the positive column of the discharge.

Of course, it is not necessary that ionization processes in the high frequency discharge be very efficient since the only way ions can disappear is by recombination or diffusion to the walls. The same cannot be said of the excitation processes, however, for the intensity of the light produced in the positive column is quite comparable with the intensity of the light emitted by the positive column of an ordinary Geissler tube carrying the same current. The only source of high velocity electrons imaginable is the region under the electrodes; but it is hard to believe that these electrons should be responsible for all the ionization and excitation in the positive column of the discharge. The writer confesses that he is unable to suggest any reasonable solution of the problem from a consideration of the mechanics of individual electrons; whether or not an explanation of the phenomena can be worked out by considering the volume of ionized gas as a plasma has not as yet been determined.

The writer is indebted to Professor O. S. Duffendack and Professor R. A. Sawyer for advice rendered and also to Mr. J. S. Owens who assisted in the experimental work.

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twenty-eighth of the preceding month; for the second issue, the thirteenth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Diffraction of Hydrogen Atoms by the Mosaic Structure of Crystals

The de Broglie wave spectra of a beam of hydrogen atoms produced by reflection from a crystal of lithium fluoride have been photographed under conditions of improved technique with the primary features described in abstract No. 2 of the 1930 Chicago Meeting of the American Physical Society. Still more recent plates with higher resolution show another type of spectrum which will be referred to as the secondary spectrum. Although the resolution is still too low in this spectrum to separate the maximum of its wave-length distribution from the specularly reflected zero order beam, it is sufficient to show that the secondary spectrum has four branches lying in the directions corresponding to diffraction by a grating whose lines are parallel to the cleavage planes of the crystal. The fact that the maximum of the wave-length distribution is not resolved permits it to be said that the spacing of the secondary lattice is greater than 50A, and the observations are not in disagreement with a spacing of more than 100A.

These facts are believed to support Zwicky's theory of the mosaic structure of crystals (Helvetica Physica Acta **III**, 269, 1930). Although the writer is not familiar with any calculations applying to the structure of LiF the spacing of the secondary lattice of these crystals should not differ in order of magnitude from that of rock salt for which Zwicky calculates 110A.

In the experiments the crystals were heated before the exposure was started to the point that the secondary structure of the crystal might well have been developed on the surface by evaporation.

THOMAS H. JOHNSON
The Bartol Research Foundation of the Franklin Institute,
Swarthmore, Pa.,
December 2, 1930.

On Some of the New Ultra-Ionization Potentials of Mercury Vapor

In view of the recent interest in the ultra-ionization potentials of mercury vapor (A. L. Hughes and C. M. Van Atta, Phys. Rev. **36**, 214, 1930, Philip J. Smith, 166th Meeting of the American Physical Society and Curtis R. Haupt, 167th Meeting of the American Physical Society) I would like to call attention to some observations of Mr. R. D. Potter, made at Duke University under my direction and published in the Journal of the Elisha Mitchell Scientific Society, **44**, 31, 1928. Inasmuch as the results of the experiment described in this paper do not seem to have come to the attention of other workers in this field, a brief statement of the results may be of interest.

Electrons from a tungsten filament were projected parallel to the axis of a tube and were collimated by means of a coaxial magnetic field of approximately 250 gauss. Collisions between electrons and mercury atoms occurred in a space midway between two rows of parallel and plane electrodes symmetrically placed with respect to the electron beam. A small electric field between these plates served to draw out positive ions formed in the region of the beam. The electrons after passing between the sets of parallel plates were collected by an electron trap. An accelerating potential of 125 volts inside the electron trap made it a good absorber of electrons. Since the primary electrons were collimated into a beam by the magnetic field they did not strike the edges of the slits in the accelerating plates. This prevented the formation of secondary electrons.

The procedure was to measure the saturated positive ion current and total electron

current for successive values of the accelerating potential, observations being taken at 0.10 volt intervals.

A plot of the ratio of positive ion to total electron current showed a series of abrupt changes in slope which resembled the familiar ones of Franck and Einsporn rather than those reported by J. C. Morris (Phys. Rev. **32**, 447, 1928). Critical potentials were observed at 10.40, 10.66, 11.00, 11.41, 11.72, 12.06, 12.40, 12.80 and 13.25 volts. The values given have been corrected for initial thermal energies, etc., by assuming the potential at which ions were first detectable to be 10.40 volts.

An examination of the results indicates that in the main there is good agreement between the above critical ultra-ionization potentials and those reported in subsequent work mentioned at the beginning of this letter.

WALTER M. NIELSEN
Bartol Research Laboratory of the Franklin Institute,
Swarthmore, Pa.,
December 2, 1930.

Projective Relativity and the Quantum Field

A recent paper[1] by O. Veblen and the present writer showed that the "five-dimensional" relativity theory of Kaluza and O. Klein is to be regarded as a four-dimensional projective theory; a natural generalization of the formalism from this point of view led to a set of field equations which contained not only gravitational and electromagnetic field equations as in the usual relativity theory but also the relativistic Schrödinger equation.

The formalism was based on the symmetric projective tensor $G_{\alpha\beta}$ which may be decomposed as

$$G_{\alpha\beta} = \gamma_{\alpha\beta}\Phi^2 = (\delta_\alpha{}^a\delta_\beta{}^b g_{ab} + \phi_\alpha\phi_\beta)\Phi^2,$$

as explained in P. R.

I have been able to obtain a set of four-dimensional projective field relations which is to the field relations of P. R. what the Dirac wave equation is to the relativistic Schrödinger equation.

The basic quantity of space-time is taken to be a projective vector, H_α, of index N with which is associated one of zero index denoted by h_α. The components of these vectors are not assumed to obey the commutative law of multiplication; they may be regarded as matrices. The restrictions are imposed that

$$H_\alpha H_\beta + H_\beta H_\alpha = 2G_{\alpha\beta} \qquad (1)$$

$$h_\alpha h_\beta + h_\beta h_\alpha = 2\gamma_{\alpha\beta} \qquad (2)$$

where $G_{\alpha\beta}$ and $\gamma_{\alpha\beta}$ commute with everything they multiply. $\gamma_{\alpha\beta}$ are now associated tentatively with the similar quantities of P. R.

Indices of the h's are raised by means of the γ's and the field equations are taken to be

$$h^\alpha\left(\frac{\partial H_\beta}{\partial x^\alpha} - \frac{\partial H_\alpha}{\partial x^\beta}\right) = 0. \qquad (3)$$

A realization of (1) and (2) may be obtained in terms of projective ennuples of vectors in the tangent spaces[2] and a basis consisting of five four-rowed square matrices satisfying[3]

$$E_\sigma E_\tau + E_\tau E_\sigma = 2\delta_{\sigma\tau}1.$$

Denoting the components of the vectors of an ennuple by $h_{\alpha\sigma}$ we set

$$h_\alpha = h_{\alpha\sigma}E_\sigma.$$

Realization of the H's is effected by the introduction of a one-columned four-rowed matrix, Ψ, by

$$H_\alpha = h_\alpha\Psi$$

together with a suitable definition of matrix multiplication.

With the above realization the field Eqs. (3) can be shown to contain Dirac's wave equation for a single electron as a special case (i.e. when gravitation is neglected) of the scalar part of the projective set.

If we inserted the relations

$$G_{\alpha\beta} = \gamma_{\alpha\beta}\Phi^2 \qquad (4)$$

together with (1) and (2) we would be unable to obtain a satisfactory realization on account of the difference between spatial and temporal coordinates. A realization in terms of eight-rowed square matrices for the E's avoids this difficulty but introduces the new difficulty that although the scalar part is still equivalent to Dirac's wave equation the whole set of equations numbers forty and we have merely twenty-eight functions entering them.

The Dirac equation is obtained as a special

[1] O. Veblen and B. Hoffmann, Phys. Rev. **36**, 810 (1930); referred to as P. R.

[2] See the "five-dimensional" formulation due to Zaycoff, Zeits. f. Physik **58**, 833 (1929).

[3] See for example Eddington, Proc. Roy. Soc. **A126**, 696 (1930).

case of part of a system of field relations constructed in close analogy with the system of P. R. There is thus a possibility that the complete system will constitute an improved unification within the relativity theory of the gravitational electromagnetic and quantum aspects of the field.

The complete set of field relations (1), (2) and (3) (and others not mentioned here), can be shown to be invariant under general relativity transformations.

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December 8, 1930.

Thermal Fluctuations of the Surface Potential of a Cathode as Affecting Electron Emission

There are at present two groups of thermionic phenomena in which theory and experiment lie rather far apart. These are (1) the departures of the constant A from the theoretical value, particularly in the case of surface films, and (2) the anomalously large values of the Schottky effect (increase of emission with field) which are also most marked for surface films. The following considerations offer a possible explanation of these difficulties.

Let us select a conductor, one of whose ends is a circular patch of radius r on the surface of the electron emitter, the other end being the surrounding surface. Current may flow from the patch into the underlying material and out again to the surrounding surface. We shall suppose the surface layers of the emitter to have much higher resistance than the underlying material, partly because the surface is a discontinuity, and partly because the surface may be covered purposely with contaminating layers. The resistance of our conductor will then be $R_0 = R_s/\pi r^2$ where R_s is the surface resistance per cm² encountered by electrons flowing through the surface. Our conductor is shunted by the capacity C across its end surfaces (infinite for a perfect conductor) which may reasonably be taken as of the form βr. Hence the expression for the effective resistance of our conductor at a frequency ω radians per second is

$$R = \frac{R_0}{1 + R_0^2\omega^2C^2} = \frac{R_s}{\pi r^2 + \beta^2(\omega^2/\pi)R_s^2}.$$

Johnson[1] has shown that as a result of thermal agitation there will be a mean square e.m.f. across the ends of our conductor given by

$$\bar{V}^2 = 3.48 \times 10^{-20} TR(\text{volts})^2$$

where T is the absolute temperature.

We shall take r approximately equal to the critical distance (x_m) which an electron must reach in order to escape from the surface. Hence the fluctuations of the potential of our patch will change appreciably the work function (ϕ) for the escape of electrons from the patch. These fluctuations are equally positive and negative, but since the emission (i) is an exponential function of ϕ, they will give rise to a net increase in emission (a sort of rectification action).

If i_0 is the "normal" electron emission from the patch (including the normal Schottky correction), the relative increase in emission produced by the fluctuations is found to be

$$\frac{i - i_0}{i_0} = 2.41 \times 10^{-12}\frac{R}{T} = \alpha\frac{R}{T}. \qquad (1)$$

The surface may be regarded as made up of a number of such patches, so that the emission from the whole surface will be given by an expression like that above.

For the fluctuation effect to make an appreciable change in emission, the term $\alpha R/T$ must be at least of the order one tenth. If we consider the pure resistance part of R only, and remember that r is of the order 10^{-4} cm, we find that R_s must be of the order 100 ohms/cm². There appears to be no definite experimental evidence against the existence a surface resistance of this order in vacuum. Experiments are projected for measuring this surface resistance and its temperature coefficient. Ionization effects at the surface must modify this resistance in the case of anodes in gas discharges.

The anomalous Schottky effect has been discussed recently by Langmuir.[2] To compare our theory with this effect we form the partial derivative

$$\frac{\partial \ln i}{\partial (F)^{1/2}} = \frac{4.39}{T} + \frac{\alpha}{T + \alpha R}\frac{\partial R}{\partial (F)^{1/2}}. \qquad (2)$$

For weak fields the critical distance is large, r is large, and R approaches zero. Hence

[1] J. B. Johnson, Phys. Rev. **32**, 97 (1928).
[2] I. Langmuir, Reviews of Modern Physics **2**, 150 (1930).

$\partial R/\partial(F)^{1/2}$ is zero, and we have the normal Schottky slope. This is the region in which Nottingham's[3] emission measurements at zero field lie, and also Langmuir and Kingdon's[4] measurements of contact potential. The effect we are considering is absent in this range. As the field is increased, the critical distance decreases, r decreases, R increases, and the increase in $\partial R/\partial(F)^{1/2}$ gives an increased Schottky slope. Finally for very large fields the term involving r in R becomes negligible, and the effective resistance of our conductor becomes independent of the field. Hence $\partial R/\partial(F)^{1/2}$ approaches zero, and the slope approaches the normal Schottky value, as observed.

If we measure the Schottky slopes for ThW at moderately strong fields and for different filament temperatures, we find that the departure from the normal slope is greatest at the lowest temperatures (reference 2, page 156). This is in agreement with the occurrence of the factor $(T+\alpha R)$ in the denominator in Eq. (2).

It is evident that the introduction of a surface resistance, which will vary with temperature, may be made to account for the observed vagaries of the emission constant A by a suitable choice of the temperature coefficient of this resistance. It is hardly profitable to discuss this point without some experimental knowledge of these surface resistances.

In conclusion we may note that these thermal fluctuations of surface potential are perhaps connected with the "flicker" effect.[5] It is evident that such a theory would bear some resemblances to the theory of this effect advanced by Johnson[5] and developed by Schottky,[6] which ascribes the flicker to fluctuations in the composition of the surface. In our case the frequency variation of the effect would be introduced by the variation of R with frequency, the fluctuations of surface potential presumably approaching a maximum value as ω is decreased.

It is hoped to discuss these questions in more detail later, particularly if some experimental evidence can be obtained about the surface resistance and its temperature coefficient.

The writer is indebted to Dr. Langmuir and to Dr. Tonks for discussion of these ideas.

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December 3, 1930.

[3] Nottingham, Phys. Rev. **36,** 386 (1930).
[4] I. Langmuir and K. H. Kingdon, Phys. Rev. **34,** 129 (1929).
[5] J. B. Johnson, Phys. Rev. **26,** 71 (1925).
[6] W. Schottky, Phys. Rev. **28,** 74 (1926).

Mean Value Theories in Quantum Mechanics

It is known[1] that in some cases there exists a close connection between the equation of classical dynamics and corresponding relations between mean values of quantities in quantum mechanics. Thus, for instance, it has been shown by Ehrenfest that according to Schroedinger's non-relativistic equation the mean momentum $\bar{p}$ is related to the mean position $\bar{q}$ by $\bar{p}=m\dot{\bar{q}}$ and also that the rate of change of the mean momentum $\bar{p}$ is equal to the mean of $-\text{grad } V$ where V is the potential energy. This theorem has also been generalized to more dimensions by Ruark. While it is satisfactory to see the similarity of classical and quantum relations in such special instances it is nevertheless desirable to bear in mind also a somewhat more general point of view. It is readily seen that according to the transformation theory the reason for the validity of mean value theorems is that the equations of classical theory hold, in the above instance, also in the quantum theory between corresponding matrices. Thus as a consequence of the Hamiltonian form $H=p^2/2m+V(q)$ we have $p=m\dot{q}$, $\dot{p}=-(\partial V/\partial q)$ holding as equations between matrices. If we refer all the matrices to the same reference system e.g. that of q and if we write the probability amplitude as $S(q')$ then we also have

$$\int S^*(q')\dot{p}(q',q'')S(q')dq'dq'' = m(d/dt)\int S^*(q')q(q'q'')S(q'')dq'dq''$$

or

$$\bar{p} = m\dot{\bar{q}}.$$

We are allowed to use here the equation

$$\frac{d}{dt}\int S^*(q')q(q',q'')S(q'')dq'dq'' = \int S^*(q')\frac{d}{dt}q(q',q'')S(q'')dq'dq''$$

[1] P. Ehrenfest, Zeits. f. Physik **45,** 455 (1927); A. E. Ruark, Phys. Rev. **31,** 533 (1928).

because (1) we may work with $S(q')$ independent of t provided the matrix $q(q', q'')$ involves t as a parameter, (2) the equation is obviously true in the reference system of the energy where $q_{nm}(t) = q_{nm}(0) \exp[(2\pi i/h)(W_n - W_m)t]$ (3) the values of the integrals on the right and left of the above equation are indepedent of the reference system used for matrix representation. In a similar way we have

$$\frac{d\bar{p}}{dt} = \bar{\dot{p}} = -\frac{\overline{\partial V}}{\partial q}.$$

The way in which we use the matrices $q(q', q'')$ is explained very clearly in Schroedinger Sitzungsberichte der preussischen Akademie XXIV p. 417, 1930, and is treated in Weyl's book, chapter II section 15. Remembering that Schroedinger's $\psi(0)$ is our S, it is seen that at any time the averages $\overline{\partial V \partial/q}$ is taken weighing every element of the configuration space in proportion to $\psi^*(t)\psi(t)$ at that point at the particular time i.e. the average is taken in the same way as by Ehrenfest and Ruark. The same can be done for *any other equation which holds between matrix as well as classical quantities.* The only doubtful point of this shorthand proof lies in dealing with singular matrices which must be expressed by means of the δ function. This however, is usually only a formal objection since throwing away the "surface integral" contributions of partial integrations is also a necessary part of the purely wave-mechanical proof such as that of Ehrenfest quoted above.

Although the above statement is simple enough to be called trivial it seems that its physical implication is not always realized. Thus for instance the motion of a non-relativistic spinless electron in a magnetic field is governed by the same equations in quantum and in classical dynamics. The center of mass is therefore moving as the classical center of mass under the action of the mean electromagnetic field in the wave package. This has already been proved a long time ago by Kennard and elucidated by Eckart in connection with a recently suggested explanation of discrepancies between the values of e/m. Similarly with the relativistic Dirac equation the rate of change of the mechanical momentum is known to be given by a formula having the same structure as the classical formula, the classical velocities being replaced by $-c\alpha_i$. Again the mean value theorem holds. The equation which proves this is the one derived by Fock.[2]

$$\frac{d}{dt}(p_1 + eA_1/c) = e\frac{\partial A_0}{\partial x_1} + e\alpha_2\left(\frac{\partial A_2}{\partial x_1} - \frac{\partial A_1}{\partial x_2}\right) - e\alpha_3\left(\frac{\partial A_1}{\partial x_3} - \frac{\partial A_3}{\partial x_1}\right)$$

$$\frac{dx_1}{dt} = -c\alpha_1.$$

Here $p_1 + eA_1/c$ is the momentum in the direction x_1, A_0 is the scalar potential, (A_1, A_2, A_3) is the vector potential and α_1, α_2, α_3, α_4 are Dirac's four-row matrices. The equation proves that the rate of change of the average of $p_1 + eA_1/c$ of a wave package is related to the average force on the wave package by the equation of classical electordynamics

$$\boldsymbol{F} = \rho\{\boldsymbol{E} + [\mathbf{v}\boldsymbol{H}]/c\}.$$

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December 12, 1930.

[2] Fock, Zeits. f. Physik **55**, 127 (1929).

Block Structure and Ferromagnetism

In the following a model is proposed for ferromagnetic substance based on the assumption of the existence of a "block structure" in solids as postulated by Smekal and Zwicky, and some of the properties of this model are pointed out. In a future communication it is hoped to give a more detailed and comprehensive account of the derivations and results indicated below.

A block, according to Zwicky,[1] is a region having the properties of a perfect crystal, surrounded by a surface physically different from the volume. This difference is connected with a local rearrangement of atoms such that along the surface the average interatomic distance is not that prevailing inside of a block. If such blocks exist, it is not unreasonable to assume that each one is spontaneously magnetized as predicted by the Weiss-Heisenberg theory

$$\frac{I_T}{I_0} = \tanh\frac{\mu_B N I_T}{KT}. \qquad (1)$$

[1] F. Zwicky, Helvetica Physica Acta **3**, 269 (1930).

In this expression the dependence on H is omitted as it is negligibly small for the field strengths used in most experiments, and its inclusion would add nothing to the following discussion. μ_B is a Bohr magneton. The assumption is now made, and this is the only *new* assumption, that various blocks may be magnetized in various directions, or what amounts to the same thing, any particular block may change the direction in which it is magnetized, and its magnetic moment need not be parallel to those of its neighbors. This is equivalent to saying that the electrons on opposite sides of a block surface are not ferromagnetically coupled to each other. Such a situation is not unthinkable, as such a coupling depends on Heisenberg's resonance integral which is known to be extraordinarily sensitive to variations in inter-atomic spacing, and such variations actually define the surface of a block.

Our model, then, is a group of permanent magnets, having primarily a thermomagnetic interaction. For the present, surface phenomena are neglected. In order to simplify the problem, the blocks are assumed isotropic, so that there are no "directions of easy magnetization." These last two assumptions should be dropped in a more exhaustive discussion. Under these conditions the blocks may be expected to interact in such a way that the magnetization is approximately given by

$$\frac{I}{I_T} = \coth x - \frac{1}{x} \qquad x = \frac{\mu}{KT}(H + LI). \quad (2)$$

Here μ is the block moment and is given by $I_T v$, the saturation intensity at the temperature T multiplied by the volume of a block. L is a factor varying between 0 for long thin blocks whose axis is parallel to H, and 4π for disk shaped blocks. LI represents the internal field. Eqs. (1) and (2) define the behaviour of our model.

The first point of interest is that this model is essentially that of Ewing, with the exception that the elementary magnets, instead of being of atomic dimensions, are somewhat larger. Thus the model is fundamentally capable of describing a magnetization curve and a hysteresis loop, as Ewing demonstrated experimentally. The details are determined by the only two arbitrary constants, appearing in the equations, μ and L. To get an idea of their order of magnitude it is possible to assign values to them which will give observed values for K_0, the initial susceptibility. Using experimental data obtained on iron, nickel and cobalt for K_0 and I_0, and substituting extreme values of L, we find that the block volume contains between 10^2 and 10^6 atoms. An intermediate value of L would give an intermediate block size.

The next point of interest is that this model gives the approach to saturation correctly. In a very thorough investigation Weiss[2] showed that most substances approach saturation according to the formulae

$$I = I_T(1 - a/H) \quad (3)$$

$$I_T = I_0(1 - AT^2). \quad (4)$$

The first of these formulae follows immediately from Eq. (2), and from the constant a it is possible to compute the number of atoms per block. ($a = KT/\mu$; $\mu = vI_T$). With Weiss's data for nickel and iron we get approximately 10^5 atoms per block. Weiss examined the approach to saturation as a function of the temperature between 100°K and 300°K. In this region I_T/I_0 as given by Eq. (1) is very approximately a straight line if plotted as a function of T^2. From the constant A it is possible to compute the molecular field constant N, and the values obtained are quite reasonable. It is true that an extrapolation of (4) for $T=0$ leads to somewhat too high values for I_0, but in general the error so committed will be small.

Further, this model has two Curie-points, a property of most ferromagnetic substances as pointed out by Forrer.[3] θ_p the paramagnetic Curie-point is defined by the modified Curie Equation $x = c/(T-\theta_p)$ for $T > \theta_p$. θ_f, the ferromagnetic Curie-point is in general less than θ_p, and is the temperature at which spontaneous magnetization disappears. θ_p is given in the usual way by Eq. (1). On the other hand Eq. (2) will itself have a Curie-point

$$\theta_f = \frac{\mu L I_T}{3K}.$$

That is, for $T > \theta_f$ the spontaneous magnetization of the whole material[4] will disappear, whereas for $T > \theta_p$ the blocks themselves lose their moments. From this it is evident

[2] P. Weiss, Ann. de Physique **12**, 20 (1929).

[3] R. Forrer, Journ. de Ph. et le Rad. **1**, 49 (1930).

that $\theta_f]_{T=\theta_f} < \theta_p$ as it is actually observed in most substances. A detailed examination shows that $\theta_p - \theta_f =$ approximately 15°C is consistent with blocks containing about 10^5 atoms.

Such an interpretation of θ_f brings with it the necessity of a new explanation of the thermal phenomena at the Curie-point. Such an explanation it is impossible to give until more definite assumptions can be made regarding the surface energies of the blocks, the effect of strains, etc. The fact that acceptance of the proposed model would require the abandonment of our present explanation of thermomagnetic phenomena at the Curie-point, would be a telling argument against such a model, were it not that just here the Weiss Theory is in part not quite satisfactory (in its interpretation of the change in specific heat for $T=\theta$) and in part purely thermodynamic (in the relationship it establishes between the specific heat and the magnetocaloric effect).

In conclusion I wish to point out that blocks containing approximately 10^5 atoms, as here postulated for the explanation of three ferromagnetic phenomena, are of the same order of magnitude as those postulated by Smekal and Zwicky to explain certain mechanical and electrical phenomena.

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November 19, 1930.

[4] Spontaneous magnetization of the sample need not, of course, include the whole sample. It may be spontaneously magnetized in different directions in different regions. It would be sufficient that large groups of units, in this case larger groups of blocks, should possess a resultant moment in the absence of externally applied fields.

Secondary Electrons from Molybdenum

The writer has continued work begun by Soller (Phys. Rev. **36**, 664, 1930) on the distribution in energy of electrons emitted by a molybdenum target bombarded by a narrow, homogeneous beam of electrons of relatively low energy (20 to 100 volts).

The apparatus was a modification of that of Soller, employing the method of magnetic analysis. The target was heated by electron bombardment for a total of 700 hours. Observations were taken at intervals throughout this outgassing period. With the primary energy held constant, measurements were taken of the number of secondary electrons (N_ϵ) of energy ϵ. By changing the magnetic field, ϵ was made to vary in steps of 0.1 to 0.2 volts from zero up to the primary energy. Curves were plotted for $N_\epsilon/N \times$const. as a function of ϵ where N is the total number of primary electrons.

Curves plotted from the results obtained for a cold target show, in addition to the usual large group of secondary electrons with energy approximately that of the primaries, a low maximum in the region 5 to 15 volts and a second very broad and somewhat higher maximum at an energy approximately one-half that of the primaries. For low primary energies these two groups become merged. In addition there are three well defined maxima corresponding to electrons possessing energies 4.7, 11.2, and 23.2 ($\pm$.4) volts less than the energy of the true reflection maximum. These last maxima are similar to those found by Rudberg (Proc. Roy. Soc. **A127**, 111, 1930) for various metals and indicate the presence of reflected primary electrons which have lost a discrete amount of energy in the process of reflection. The height of these peaks increases as the velocity of the primary electrons decreases. These peaks appeared only after considerable outgassing and became more and more marked with further heating.

In attempting to eliminate the effects due to gas occluded on the surface of a cold target, the following procedure was adopted. With the magnetic field set to correspond to a given value of ϵ the target was heated to a bright yellow for thirty seconds and N_ϵ measured thirty seconds after the bombarding current was cut off. (The target ceased to be visibly red after about 20 seconds.) This procedure was followed through the whole range of values of ϵ. A typical curve obtained from these data was that for a primary energy of 60 volts. Observations taken in this way show a very large group of low velocity secondaries of energy from three to twenty-five volts, and N_ϵ/N now reaches a maximum value at 8 volts which is 27 times as great as the corresponding maximum at 8 volts for a cold target. For higher values of ϵ the values

of N_ϵ/N are more nearly alike for the hot and the cold target, the ratio being 2 at a point just short of the full velocity maximum. The three discrete peaks are greatly enhanced in the case of the freshly heated target.

The large low velocity group disappears rapidly with time, the value of N_ϵ/N at eleven volts changing from 27 to 3 during the first three minutes but there is no such rapid change for higher values of ϵ. After the first three minutes there is no further change for as much as thirty minutes, following which there is a gradual decrease over a period of three or four hours. The gradual decrease after 33 minutes is believed due to the occlusion of gases. The first rapid decrease is of unknown origin but, since it is independent of pressure and occurs in such a short time, it does not seem possible that it can be due to the adsorption of gas. The best vacua were of the order of 10^{-7} mm of Hg.

In addition curves were plotted for the height of the full velocity peak as a function of the primary velocity. These show marked minima at 9.3 and 20.6 volts. The difference between these is 11.3, about the same as the difference between the values of ϵ for the 11.2 and 23.2 volt discrete energy-loss maxima. Corrections for work functions etc., necessary to bring 9.3 and 20.6 into agreement with 11.2 and 23.2 are not unreasonable. The full velocity data were not reliable for primary voltages below 6 volts so that no check was obtained for the 4.7 discrete loss group. It is suggested that these minima in the number of elastically reflected electrons are due to some sort of excitation within the metal, the efficiency of which increases as the energy of the primary electrons approaches that necessary for the excitation. On this assumption the three discrete groups of secondaries are composed of reflected primary electrons which have lost a definite amount of energy in the process of reflection.

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December 20, 1930.

On Collisions of Photons

According to the modern concepts of matter and energy, practically all the properties which are usually attributed to matter, can be associated with radiation. The source of solar and stellar energy can be traced to the "annihilation" of matter. However it is not certain that energy is transformed into matter, but with the help of this hypothesis it is possible to calculate correctly the relative mass of the elementary particles of matter. The identity of matter and energy would thus appear to be almost complete and the principles of the conservation of mass and of energy to be but two aspects of one universal principle.

Following up these considerations one would naturally be led to expect the existence of mutual collisions of photons. Thus the paper "Attempt to Detect Collisions of Photons" by Hughes and Jauncey, which appeared in Physical Review **36**, 773, 1930, is of special interest.

About two years ago this same idea occurred to me and I communicated it to Professor G. Angenheister, Director of the Geophysikalisches Institut, Göttingen, in whose laboratory I was working at the time. But the resources of that institution were not adequate to an experimental verification of the idea. The nature of the effect which I expected was similar to that expected by Hughes and Jauncey. In the calculations regarding the possibility of observing the effect, the faintest star clearly visible by the naked eye, was taken to be of the sixth magnitude, as is usually assumed. Using Zöllner's estimate of the ratio of the magnitude of the sun and Capella (magnitude 0.2) and using Exner's value for the vertical illumination of the sun, the limit of human vision was calculated to be 3 millimicrolux. The sensitivity of the eye is maximum for the frequency 0.58×10^{15}, the quantum of which is 3.8×10^{-12} erg. So the number of quanta received by the eye when receiving the minimum visible light is about 360 per second. This number seemed to be too high to be obtained by the scattering of photons due to the mutual collisions which one would expect at the point of crossing of two beams of light under ordinary conditions. I concluded that the expected effect could not possibly be detected with certainty by an optical method, visual or photographic. (A selenium detector might be better suited for the purpose). My plan, therefore, was to look for the theoretically expected effect with the help of some instrument that would record the elementary effect of single photons and not simply the integrated effect of a multitude. Such

an instrument I recognized in the "Elektronenzählrohr" or even in the so-called "Glimmlampe." For this purpose I wanted to utilize the "Elektronenzählrohren," which I had constructed (with the collaboration of K. Wölcken) primarily for the investigation of gamma and cosmic rays.

Instead of using ordinary light (as Hughes and Jauncey have done) my intention was to use x-rays or gamma-rays, but I could not put my intention into practice for lack of necessary equipments. The negative result of Hughes' and Jauncey's experiment need not necessarily lead to the conclusion that mutual collisions among photons do not occur. Those who have the advantage of a good physical laboratory, may find it worthwhile to try the experiment on the lines indicated above.

In conclusion, I would like to mention that sometime ago I found out that the theoretical possibility of the existence of the nature of the effect in question was pointed out by L. de Broglie as early as 1926 in his book "Ondes es Mouvements" pp. 96–98 (Gauthier-Villars, Paris).

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November 11, 1930.

BOOK REVIEWS

Optical Rotatory Power A general discussion held by the Faraday Society. Pp. 198. Aberdeen University Press, 1930. Price 10s 6d.

The contributions to this discussion cover practically all phases of the subject and are grouped under the following headings:

I. The Physical Basis of Optical Rotatory Power (8 papers)
II. Apparatus and Methods (2 papers)
III. The Rotatory Power of Solutions (7 papers)
IV. The Chemical Aspects of Optical Rotatory Power (4 papers).

A considerable portion of the discussion centers about the physical theories of optical activity which are presented in articles by Kuhn, Malleman, Ewald, Temple, and others. The wave mechanics of rotatory polarization is shown to be at present in an unsatisfactory state, the principal short-coming being the lack of a connection between optical activity and structure. Experimental methods especially applicable to the ultra-violet region of the spectrum are reviewed by Descamps. As is shown by Cotton and others, this region of the spectrum is an important one in the study of rotatory dispersion and circular dichroism. Many interesting compounds are discussed in the chemical part of the report.

J. VALASEK

Röntgenographie der Metalle und ihrer Legierungen. M. C. NEUBERGER. Pp. 278, figs. 66. Price RM 25.

This book is a fit companion volume to the author's excellent *Röntgenographie des Eisens und seiner Legierungen*, which appeared about a year ago. Because of this previous work, the author confines himself in the present volume to a treatment of the non-ferrous metals and alloys in the light of x-ray data.

The present work supplies a long-felt want in that it renders available at hand in one volume a mass of x-ray data relating to metals and alloys, which is widely scattered, and which can otherwise be obtained in case of need only by an extensive searching of the literature. These data are critically discussed by the author and, wherever a structure is in dispute, he gives not only the result which he considers as probably correct, but also the conflicting results of other workers. A liberal use of tables of x-ray data and reproductions of original x-ray photographs add to the value of the book.

WILLIAM P. JESSE

Les Applications des Rayons X. J. J. TRILLAT. Pp. 298, figs. 108. Les Presses Universitaires de France, Paris, 1930. Price, 85 francs.

This book, as the title indicates, is written for the benefit of the rapidly growing group who would know something of the recent developments of x-rays as a tool in physics, chemistry and metallurgy. With this practical end in view, the author avoids as much as possible all theoretical aspects of the subject which do not bear directly on the technical uses of x-rays and frequently discusses in detail manipulative methods which may prove valuable to one contemplating work in this field.

The book is divided into two sections. In the first of these, which comprises the first third of the book, the author has an introductory chapter on the elementary principles of crystal structure and of x-ray diffraction. Then follows an extended discussion of various types of x-ray tubes and apparatus and a survey of the different methods of x-ray spectroscopy.

The second part of the book deals with recent advances in the use of x-rays in widely different fields. The first chapter on the metals, while not entirely comprehensive, is probably as complete as the enormous mass of work on the subject will allow in such a limited space. This chapter is followed by a very good account of work on the long chain carbon compounds, the material for which is in a large part taken from the author's own researches. The following chapters deal with cellulose and its derivatives, rubber and resins, the diffraction of x-rays by liquids and a short discussion of colloids. The last section makes a very brief mention of radio-

graphic applications to metals and of chemical analysis by x-rays. A very good bibliography at the end of each chapter is a valuable feature of the book.

The book is clearly written and is by an author who has added something to almost every field discussed. It should prove valuable to anyone interested in the technical uses of x-rays.

WILLIAM P. JESSE

The Principles of Quantum Mechanics. P. A. M. DIRAC at the Clarendon Press, Oxford, 1930. Pp. 257.

A book on quantum mechanics written by Dirac must be of great and in many ways unique interest to physicists. The quantum mechanics of today is not the work of one man; but since the foundation of the theory by Heisenberg and Schroedinger, there have been few cardinal advances which have not been made by Dirac; and in his papers alone one may find the key to the solution of almost any problem which the theory is competent to treat. The fact that a book on quantum mechanics must necessarily be largely an account of Dirac's own work, assures us that his account will be unitary and coherent, and that it will be given in just those terms which have shown themselves most useful to the understanding and the development of the theory.

The title of the book tells us that we shall not find here the detailed solution of many specific problems; what we do find is the development and exposition of the methods by which such problems may most simply be attacked. In this respect Dirac's book is very complete—for so short a book, astonishingly complete. In many cases the methods used by Dirac are considerably simpler and more direct than any to be found elsewhere; this is true of his treatment of angular momentum, of the theory of collisions and of radiation, and of the theory of systems containing similar particles. In this last problem, it is true, Dirac's method does not give Wigner's complet *e* reduction of all matrices; and this renders the application of his method to many problems unnecessarily laborious. A few developments of theoretical significance are not included in the book; of these omissions, possibly the most important are the theory of quantized waves for systems satisfying the exclusion principle, the unitary theory of electromagnetic field and matter, and the theory of the electron in a gravitational field. But these things belong perhaps rather to the quantum mechanics of the future; and their omission will hardly be found to diminish the value of the book.

In some very fundamental respects Dirac's book is like Gibbs' "Elementary Principles of Statistical Mechanics": it is clear, with a clarity dangerous for a beginner, deductive, and in its foundations abstract; its argument is predominantly analytical; the virtual contact with experiment is made quite late in the book. The difficulty which this would present for many readers is largely reduced by Dirac's introductory descriptive chapter, and by conscientious efforts to translate all results into physical terms. But physical ideas are seldom used to advance the argument, and occur chiefly as an aid to exposition. The book remains a difficult book, and one suited only to those who come to it with some familiarity with the theory. It should not be the sole text, nor the first text, in quantum theory, just as that of Gibbs' should not be the first in statistical mechanics. Every part of the theory may be understood from more than one point of view; to see it always and only from one point of view, even if that be the most general, is to understand it only partially.

We must say a few words of Dirac's quasi-postulate-theory foundation of the quantum mechanics. Dirac begins his argument by introducing certain symbols, said for picturesqueness to "represent" states and observable variables of a system, and by laying down axioms for the manipulation of these symbols. These symbols do not represent, as do those more current in mathematical physics, a class of numbers defined by some specific measurement on a system; they represent the class of such classes of numbers, defined by any measurement on the system. Thus Dirac's axioms,—and, in fact, most of his earlier chapters—have an extreme generality; but because the meaning of any equation, in physics, is ultimately to be derived from the numbers given by specific observations, they have also a higher grade of abstractness. This is the price that must be paid for the generality. And Dirac's book will be for many of us so satisfying, that we shall be glad to pay it.

J. R. OPPENHEIMER

PROCEEDINGS OF THE AMERICAN PHYSICAL SOCIETY

MINUTES OF THE CHICAGO MEETING, NOVEMBER 28 AND 29, 1930

The 166th regular meeting of the American Physical Society was held in Chicago, Illinois, at the Ryerson Physical Laboratory and Eckhart Hall of the University of Chicago on Friday and Saturday, November 28 and 29, 1930. The presiding officers were Professor Henry G. Gale, President of the Society, Dr. W. F. G. Swann, Vice-president and Professor O. M. Stewart.

On Friday evening the Physical Society had a dinner at the Hotel Windermere. There were one hundred and ten present. President Gale presided. The after dinner speakers were Dr. A. J. Dempster, Dr. Paul D. Foote, Dr. Herbert E. Ives, Prof. R. Ladenburg, Prof. M. von Laue and Professor R. Scherrer.

At the regular meeting of the Council held on Friday, November 28, 1930 at 10:30 a.m. seventy were elected to membership. *Elected to Membership:* John M. Aitchison, Gerald M. Almy, W. N. Arnquist, John V. Atanasoff, Michael Balas, Willard H. Bennett, J. C. Betz, Paul H. Boots, Robert A. Boyd, James M. Bradford, Maurice J. Brevoort, H. T. Byck, R. W. Carson, Lawrence H. Cook, Winston Cram, C. F. DeVoe, Laurance H. Donnally, J. S. Evans, Robley D. Evans, George Forster, Amelia Frank, Wendell H. Furry, Otto Halpern, R. R. Hancox, Helen Harms, H. Harold Hartzler, Arthur B. Hersey, D. M. Hill, Joseph O. Hirschfelder, Winston L. Hole, Walker Kinkaid, John R. Kerry, William S. Klein, Emeran J. Kolkmeyer, M. R. Krasno, Jules A. Larrivee, Rose LeD. Mooney, Robert Morgan, John M. Nordquist, M. Ostrofsky, Ralph G. Owens, Lyman G. Parratt, R. W. B. Pearse, W. D. Phelps, Lloyd B. Phillips, E. R. Piore, Frank W. Pote, Kurt F. Ritzau, Edward R. Schmid, Frederic A. Scott, Robert Serber, Robert S. Shankland, J. A. Sharpe, J. H. Simons, Albert Smith, Chauncey G. Suits, Shinji Togo, Philander B. Taylor, Melvin C. Terry, Rayen W. Tyler, Oliver G. Vogel, John H. Wanamaker, Mary D. Weber, Donald F. Weekes, George L. Weil, M. F. Weinrich, Lester V. Whitney, Violet Wu, H. M. Zenor and George E. Ziegler.

The regular scientific session consisted of fifty four papers, eight of which —Nos. 17, 18, 20, 26, 32, 33, 43 and 46—were read by title. The abstracts of these papers are given on the following pages. An AUTHOR INDEX will be found at the end.

W. L. SEVERINGHAUS, *Secretary*

1. Measuring the intensity of molecular beams. A. ELLETT AND R. M. ZABEL, *University of Iowa*. A sensitive Pirani gauge has been developed and used to measure the intensity of a molecular beam defined by 0.5 mm circular openings 22 mm apart. The gauge is situated 35 mm from the last opening. A beam of air gives a galvanometer deflection of 1000 cm with a pressure of 1 mm behind the first opening. H_2 produces a deflection of 2000 cm. The galvanometer sensitivity is 11.6 mm per micro-volt. The time lag of the gauge is less than the period of the galvanometer (7 seconds). The limits within which the beam forming system may be expected to give a Maxwellian distribution of velocities are discussed. The final pressure in the gauge due to a given beam depends upon the size of the gauge opening as kinetic theory predicts. The reduction in intensity of beams of air and H_2 by collision with either air or H_2 present in the experimental chamber at various pressures has been measured. The data show that the gauge may be used to measure mean free paths and to obtain more detailed information that has previously been possible as to the probability of scattering through various angles by collision.

2. Diffraction of atomic hydrogen. THOMAS H. JOHNSON, *Bartol Research Foundation, Swarthmore, Pa.* Improvements in the technique of photographing the de Broglie wave diffraction patterns, produced by the reflection of a beam of atomic hydrogen from a cleaved crystal of lithium fluoride, have considerably increased the intensity of these patterns over that of the patterns previously reported. In consequence, new features have been recorded. The patterns obtained by reflection at normal incidence consist (a) of four intense lines radiating from the central specularly reflected spot in directions perpendicular to the two mutually perpendicular sets of rows of similar ions on the surface of the crystal and (b) of four relatively weak, but plainly visible, lines radiating from the same point but perpendicular to the two sets of diagonal rows of alternately dissimilar ions. The gradation of intensity along the "*a*" lines corresponds to the dispersion of the various wave lengths of the Maxwellian velocity distribution by the grating whose lines are the rows of similar ions spaced at intervals of 2.83A. The "*b*" lines have a greater dispersion corresponding to the closer spacing of 2.00A between the rows of alternately dissimilar ions. Similar patterns observed at 45° incidence appear with branches corresponding to the various combinations of the values of 0, -1, $+1$ for m and n in the plane grating formulae $\cos\phi_0-\cos\phi=m\lambda/d$ and $\cos\theta_0-\cos\theta=n\lambda/d$.

3. The value of e/m by deflection experiments. G. E. UHLENBECK AND L. A. YOUNG, *University of Michigan*. To clarify the discussion as to whether or not a quantum mechanical treatment of the motion of electrons in magnetic fields will lead to a formula for e/m, differing from that obtained by classical electrodynamics the following problem was solved. A uniform magnetic field in the z-direction exists in the half-space $x>0$. A plane monochromatic de Broglie wave, travelling in the positive x-direction representing electrons of arbitrary energy, impinges normally on the plane $x=0$. Solutions of the wave equation were found fulfilling appropriate boundary conditions at the plane $x=0$. Currents are calculated quantum mechanically and compared with the corresponding classical expressions. It was found that for electrons possessing energies of the order of magnitude used in deflection experiments, no *observable* deviations from classical results are predicted. Another quantum mechanical effect is diffraction at slits. Simple approximate calculations show that this effect can produce a fractional error in e/m of the order of the de Broglie wave-length divided by the slit width. These results are opposite to the conclusions reached by Page (Phys. Rev. **36**, 444). We may remark that he solved a problem of "stationary states" which does not represent the actual experiments.

4. The diffraction of an electron-wave at a single layer of atoms. M. v. LAUE, Visiting Professor from the University of Berlin. (Introduced by A. H. Compton). This paper undertakes to estimate the influence of the gradual transition between the field exterior to, and in the interior of a crystal, on the diffraction of electrons. This gradual transition is required by electrostatics. The result is that this influence may be neglected for electrons whose energy is two-hundred volts or more. One can then treat the transition as discontinuous. In the case of slower electrons it seems doubtful if such a treatment is permissible.

5. Frequency variations due to the electrodeless discharge. J. T. TYKOCINER AND J. KUNZ, *University of Illinois.* Experiments were carried out to show that an oscillator which excites electrodeless discharges undergoes variations of its frequency due to the reaction of the discharges. These variations were measured by means of a heterodyne method and the results were applied for a study of the intensity and character of the electrodeless discharge currents. The fact was thus disclosed that contrary to a relation calculated on the basis of J. J. Thomson's theory of the ring discharge which demands an increase of frequency, the "ring" discharge causes a decrease of frequency. An extension of the theory was undertaken which takes into account the effect of the capacitance of the excitation coil itself and of the influence of the ionized dielectric in the discharge tube subjected to the action of electrostatic fields. It can thus be shown that due to the electrostatic forces always predominating over the electromagnetic induction, a decrease of frequency must result, whenever the inner conductance of the discharge is small enough to suppress the formation of ring discharges.

6. Interpretation of negative volt ampere characteristics of neon positive column. CLIFTON G. FOUND, *General Electric Co., Schenectady, N.Y.* The voltage gradient in the positive column of a discharge in neon decreases rapidly with increase in current. The decrease in gradient runs parallel to the increase in concentration of metastable atoms and to the increase in light efficiency. Moreover, observations show that the electrons in the positive column have velocities corresponding to a Maxwellian distribution in which electrons with a velocity greater than the resonance potential are absent. This deficiency of electrons with energy sufficient to produce ionization indicates that the positive ions are not formed by a single electronic collision but must be the result of a two stage process such as ionization of metastable atoms by slow electrons. These characteristics indicate that the negative resistance of the positive column is connected with the presence of metastable atoms. This assumption permits an explanation of the inductive impedance of a hot cathode neon tube as measured by W. F. Westendorp by a method which will be described in the near future.

7. The efficiency of ionization of mercury vapor by electron impact near the ionization potential. PHILIP T. SMITH, *University of Minnesota.* Direct measurements of the efficiency of ionization by electron impact, using an electron beam with a very narrow velocity distribution show a series of discontinuous changes in the slope of the efficiency curves as the energy of the impacting electrons is increased. Most of these discontinuities or "ultra-ionization potentials" agree with those previously observed by E. O. Lawrence, (Phys. Rev. **28,** 947 (1926)) and A. L. Hughes and C. M. Van Atta, (Phys. Rev. **36,** 214 (1930)), although several new ones have been observed. Lawrence's values were 10.40, 10.60, 11.29, 11.70, 12.06 volts. Hughes' and Van Atta's 10.40, 10.62, 10.88, 11.28, 11.40, 11.77, 12.16, 12.76. Our values, 10.40, 10.60, 10.76, 10.88, 11.07, 11.27, 11.40, 11.55, 11.70, 11.78, 11.90, 12.06, 12.17, 12.38.

8. Doppler effects in hydrogen with canal rays of uniform velocity. H. F. BATHO AND A. J. DEMPSTER, *University of Chicago.* Positive ions were produced by bombarding hydrogen with low voltage electrons from a hot cathode. The ions formed passed beside the cathode into a strong field where they were accelerated by potentials up to 15,000 volts. The ions then passed into an observation chamber, where the light emitted by the accelerated particles was photographed with a large three-prism spectrograph. With the usual canal-ray tubes broad displacements are obtained as Doppler effects due to the velocity distributions in the ions, maxima are sometimes present suggesting ions of various masses, and the observed displacement is always considerably less than that calculated from the potential difference on the tube. With the present tube sharp displaced lines of the Balmer series are obtained indicating homogeneous velocities, the displacements agree with those calculated from the potential for atomic ions, molecular ions and triatomic molecular ions. These ions break up in the observation chamber giving hydrogen atoms which emit the Balmer series lines with Doppler effects corresponding to the velocities of the ions. At low pressures the displaced line due to the molecule ion becomes the strongest as suggested by previous experiments on the positive-ray analysis of ionization products.

9. A study of the velocities of ions formed in nitrogen by electron impact. W. WALLACE LOZIER, *University of Minnesota.*—In a recent paper (Phys. Rev. **36,** 1285 (1930)) there was described a method which is suitable for a measurement of the velocities of ions formed in molecular gases by electron impact. This method is employed in a study of nitrogen. Above 35 volts electron velocity there are two groups of ions, these being N_2^+ and N^+. The N_2^+ ions possess very little kinetic energy while the majority of the N^+ ions possess about 3.0 equivalent volts velocity, these latter ions resulting from dissociation of molecular ions. The number of N^+ ions increases so rapidly with electron velocity that at about 60 volts electron velocity they actually occur in greater numbers than the N_2^+ ions, a fact which is in striking contrast to the results obtained in hydrogen.

10. The effect of resolving power on the absorption coefficient of electrons in gases. R. RONALD PALMER, *University of Minnesota.*—The absorption coefficient of electrons in helium and in mercury vapor has been studied as a function of the geometry of the experimental apparatus. An electron beam of 0.4 mm radius was used in a Mayer type of apparatus in which the opening at the end of the scattering chamber was of variable aperture. Values of the absorption coefficient were obtained for 20, 40, 80 and 135 volt electrons over an angular aperture range of from 2° to 11° as measured from the end of the electron gun. All curves showed a definite decrease in the absorption coefficient with increase in angular aperture. These curves were corrected for the positive ion current, from the efficiency of ionization data of Bleakney and Smith, to give curves for the total number of electrons collected as a function of the size of the opening. These showed also a definite decrease with increase in aperture, corresponding to a preference for scattering to take place at small angles. In helium the curves were steeper the higher the electron velocity, whereas they were more alike in mercury vapor. From Arnot's angular distribution results it is possible to predict such a curve for 80 volt electrons in mercury vapor. The predicted curve is much steeper, showing a sixty-five per cent decrease as against a thirty-two percent decrease over the same range experimentally. This discrepancy is as yet unexplained.

11. The motion of electrons in argon. H. B. WAHLIN, *University of Wisconsin.*—The mean free path λ of electrons in argon has been determined for the case where the electrons are in thermal equilibrium with the gas, using the alternating potential method for determining mobilities. The value thus found is $\lambda = 0.385$ cm at a pressure of 1 mm. This value is 9.2 times the kinetic theory value $(4(2)^{1/2}$ times the atomic free path). The mobility curves obtained when the current is plotted against the alternating voltage definitely show the influence of the Ramsauer effect.

12. Specific resistances of zinc single crystals. E. P. T. TYNDALL AND A. G. HOYEM. *University of Iowa.*—Measurements made on fourteen single crystals prepared from Kahlbaum's best zinc by the Czochralski-Gomperz method yield values of specific resistance which verify the Voigt-Thomson symmetry relation with considerably more accuracy than has been the case previously. The scattering of results of previous observers (Bridgman, Ware) appears to have been avoided here by more careful attention to experimental conditions, particularly in the determination of cross-sectional area and its variation along the crystal rod, and in temperature control. The increase in resistance due to slight strains found by Bridgman does not exist for these crystals. The specific resistances, perpendicular and parallel to the vertical axis are: $\rho_\perp = 5.88 \times 10^{-6}$, $\rho_\parallel = 6.20 \times 10^{-6}$ ohms/cm³. For a series of 22 crystals prepared from "spectroscopically pure" zinc (from the New Jersey Zinc Co.) the values $\rho_\perp = 5.83 \times 10^{-6}$, $\rho_\parallel = 6.15 \times 10^{-6}$ are obtained. The results, however, are more scattered than for the Kahlbaum crystals, but it is believed that this may be due largely to increased experimental difficulty in handling these much more easily deformable crystals. Thus, the purer zinc shows lower values of specific resistance throughout, but the ratio $\rho_\parallel/\rho_\perp$, is the same for both 1.055.

13. Electromotive force of paraffin membranes. KARL LARK-HOROVITZ AND J. E. FERGUSON, *Purdue University.*—With the method developed by Horovitz some time ago (Proc. Vienna Acad. Sci. **134,** 345(1925)) thin films of paraffin were sealed to glass tubing of known electrode function. These paraffin films are used as one electrode in aqueous solutions of dif-

ferent ionic concentrations. Measuring the change of electro-motive force of the paraffin film as a function of the concentration of ions in the solution by using a binant-electrometer (Dolezalek), the following results were obtained: Paraffin acts as a reversible electrode in respect to cations only. It behaves in solutions of HCl, KCl, NaCl, $AgNO_3$ and NaOH like a reversible electrode in respect to any of the cations contained in the solution after a certain range of concentration has been reached. In solutions of mixtures of electrolytes, paraffin behaves like a mixed electrode, its behavior being in all respects similar to the behavior of glass as described before by Horovitz and collaborators.

14. Contact potential between iron and nickel. G. N. GLASOE, *University of Wisconsin (Introduced by C. E. Mendenhall).*—Specimens of electrolytic iron and electrolytic nickel were outgassed by intensive heat treatment in a high vacuum and the contact potential between them was measured by the Kelvin null method. Photoelectric long wave limits of the specimens were measured by using filters in the path of the light from a quartz mercury arc. The light transmitted by each filter was photographed with a quartz spectrograph immediately after each determination of the photoelectric effect. The results of the measurements made after the Fe and the Ni had been heated for 300 hours were the same as those obtained after some 750 hours of heating. The plates were heated at a temperature of about 900°C at first and then the temperature of the Fe was raised to 1000°C and that of the Ni to 1100°C with no measurable change in the values obtained for the contact potential and long wave limits. The equilibrium value of the contact potential was Fe-Ni+0.20 volt ± 0.01 volt. The long wave limit of the Fe was found to be 2646A and that of the Ni to be 2537A. The work functions of the specimens corresponding to these long wave limits are: Fe 4.662 volts, and Ni 4.862 volts. The difference in these values gives the contact potential Fe-Ni+0.20 volt.

15. On the electrical resistance of contacts between solid conductors. J. FRENKEL, *Visiting Professor from Leningrad, University of Minnesota, (Introduced by H. A. Erikson).*—A contact between two solid conducting bodies is visualized as a small gap between them. This gap can be described as a potential hill, over which the electrons, according to the wave mechanical theory, can pass even with insufficient kinetic energy. There must be in general a steady flow of electrons across the gap in both directions, the difference between the two flows being the actually observed current intensity I. The general expression of I as function of the applied potential difference is obtained and discussed for the case of two identical bodies in connection with the resistance of granular structures (thin metallic films, obtained by cathodic pulverisation) and for the case of two different bodies in connection with the rectifying (valve) action.

16. Photoelectric properties of oxide cathodes. W. S. HUXFORD, *Grigsby-Grunow Research Staff, Department of Engineering Research, University of Michigan.*—The effect of applied fields on the photoelectric work function of barium-strontium oxide cathodes has been investigated in the light of recent theories on electron emission from adsorbed metallic films. Photo-currents of the order of 10^{-11} ampere were obtained when the cathodes were illuminated by light from a glass monochromator. The potentials employed were of the order of magnitude of those commonly applied to the electrodes of radio receiving tubes. As the activation of the cathode is carried to a maximum the photoelectric threshold, as measured at room temperatures, moves towards the red end of the spectrum, and the tendency to a condition of non-saturation in the emission increases. The currents due to the electrons emitted under the action of blue light saturate better than those caused by red light. A striking dependence of the photoelectric work-function upon the applied fields has been found. In the case of one cathode, the long wave limit of the photoelectric effect occurred at 9200A with a field of 40 volts per cm and at approximately 10,800A with a field of 8000 volts per cm. A quantitative estimate is made of the modification of the intrinsic surface fields by the impressed fields.

17. Photovoltaic effects in Grignard solutions. II. R. T. DUFFORD, *The University of Missouri.*—New observations are reported which bring out several new facts about the Becquerel effect in Grignard cells. Most important among these are the behavior on closed circuit, and the remarkable effect of certain depolarizers in increasing the current obtainable; and the

evidence that at least two types of response may occur with platinum electrodes. The effect is noted in several compounds not before tested. The work was done at the Research Laboratory, Incandescent Lamp Department of General Electric Co., Cleveland, Ohio.

18. The dielectric polarization of castor oil, linseed oil and tung oil. W. N. STOOPS, *Westinghouse Research Laboratories, East Pittsburgh, Pa.* (*Introduced by C. F. Hill*).—The dielectric constants and densities of castor oil, linseed oil and tung oil have been measured over the temperature range between 100°C and their freezing points. The dielectric constant and polarization data indicate the presence of polar molecules in the oils. Accordingly the dielectric constants and densities of their dilute solutions in benzene have been measured, and the electric moments calculated by means of the Debye equation. They are 3.7, 3.0 and 2.8×10^{-18} e.s.u. respectively for castor oil, linseed oil and tung oil. From the standpoint of their molecular structure, these oils may be considered as derivatives of the triglyceride of stearic acid. The above values of the electric moment agree well with what would be expected on the basis of the accepted chemical composition of the oils.

19. Orientation of hydrocarbon crystals by an electric field. RALPH D. BENNETT, *University of Chicago.*—Ewing has shown (Phys. Rev. **36,** 378 (1930) that as regards scattering power for x-rays an electret consisting of a mixture of different waxes is anisotropic. The writer has obtained results in agreement with his. Further, paraffin shows a similar anisotropy when allowed to crystallize in an electric field. Müller and his collaborators (Proc. Roy. Soc. **A120,** 437 (1928); Jour. Chem. Soc. **127,** 599 (1925); *et al.*) have shown that the normal hydrocarbon crystals have the form of thin flakes, the long axes of the molecules being perpendicular to the face of largest area. The writer's x-ray measurements indicate that the effect of the electric field is to align these crystals edgewise, i.e. the hydrocarbon chains are perpendicular to the electric field.

20. Change of frequency of x-rays scattered by bound electrons. D. P. MITCHELL AND A. J. O'LEARY, *Columbia University.*—In the Physical Review of June, 1929, one of us (D.P.M.) reported changes in wave-length of the molybdenum $K\alpha_1$ line scattered at 90° from graphite, beryllium and aluminum. These were interpreted as due to the transfer of the binding energy of K and L electrons in the scattering substances. Further investigation of this phenomenon with improved apparatus employing a background compensation method failed to disclose, in addition to the unmodified line, any of the lines previously reported. The line Mo$K\alpha_1$ was scattered from paraffin and graphite at an average angle of 90° and beryllium 154°. The experimental conditions for producing the scattered radiation were as nearly as possible like those of the earlier work. The measurements were made by means of ionization apparatus as before. However, the sensitivity and stability of the new measuring apparatus was sufficient to have disclosed such lines if their intensity exceeded 10 percent of the unmodified Mo$K\alpha_1$ line scattered from paraffin and graphite. The result is in complete accord with similar experimental work already reported by J. A. Bearden and N. S. Gingrich. Unmodified scattering by beryllium was definitely observed although quite weak. No "anti-Stokes" line was observed as previously reported. Such a line should have appeared if its intensity was 50 percent of the unmodified Mo$K\alpha_1$ line.

21. Scattering of x-rays in the neighborhood of 90 degrees. G. E. M. JAUNCEY AND G. G. HARVEY, *Washington University, St. Louis.*—X-rays from a tungsten target tube excited at 90 and 125 kilovolts were scattered by paraffin. The x-rays were filtered through aluminum so as to produce some degree of homogeniety, and the distribution of intensity amongst the wave-lengths still present was determined by an absorption method. The intensity of the x-rays scattered at the above angles by a thin slab of paraffin was calculated for each wave-length present in the primary beam, using the formulas of Dirac and Jauncey. Each wave-length was assumed to be changed on scattering by the Compton value and the proportion of the intensity of each wave-length which was absorbed in the methyl iodide in the ionization chamber was calculated. The total intensity absorbed in the ionization chamber was then found by graphical integration. In the experiment, the ratios of the intensities scattered at

75° and 120° to the intensity scattered at 97°30′ were determined. These ratios were compared with the two theoretical ratios. The agreement is much better with Dirac's than with Jauncey's formula. At the wave-lengths used Dirac's formula is not sufficiently different from the formula of Klein and Nishina for this experiment to discriminate between them.

22. Scattering of x-rays by gases. E. O. WOLLAN, *University of Chicago.*—Measurements of the scattering of x-rays by gases are in progress using a molybdenum target, with Soller slits and matched filters of ZrO_2 and SrO. This arrangement makes possible the use of more homogeneous radiation and more definitely defined scattering angles than have hitherto been reported. The intensity of scattering of hydrogen at 90° has been used as a standard with which the scattering of other gases has been compared. Due to the small intensity of scattering from hydrogen, oxygen was used as a secondary standard, with which direct comparisons of intensity with other gases was made. Measurements of the intensity of scattering from argon at angles from 10° to 90° were obtained, and put on an absolute scale by comparison with oxygen. The scattering per electron for argon was considerably greater than for hydrogen and oxygen over the whole range of angles. This indicates a strong concentration of electrons near the center of the argon atoms.

23. Electron distribution in argon, and the existence of zero point energy. ARTHUR H. COMPTON, *The University of Chicago.*—Data on the scattering of x-rays by argon, reported by Wollan are analyzed by the method recently described by the writer (Phys. Rev. **35**, 925 (1930)) The resulting electron distribution curve (U curve) shows a maximum electron density at about 0.10A from the center of the atom. The data of James and Firth (Proc. Roy. Soc. **A114**, 181 (1927)) on rock salt at 0°K give a maximum electron density of chlorine atoms at about 0.19A from the center, for 900°K at about 0.58A. The difference between the latter two values is due to the thermal motion of the atoms in the crystal. Similarly, the large difference between the radius of maximum electron density in the atoms of argon gas and of chlorine in rock salt at 0°K must mean motion of the chlorine ions in the crystal lattice. The amplitude of this motion is of the order of magnitude predicted on the quantum theory of zero point energy. This confirms the conclusion of James Waller and Hartree, who however based their conclusion on a theoretical rather than an experimental electron distribution for argon and chlorine.

24. Absorption of x-rays in gases. W. W. COLVERT, *University of Chicago.* (*Introduced by A. H. Compton.*)—X-ray spectral lines reflected from a platinum surfaced mirror and by a calcite crystal have been used for absorption measurements with neon, sulphur dioxide, chlorine and argon. The double reflection gives a more nearly homogeneous beam, since the mirror greatly reduces the higher orders of the shorter wave-lengths. The results are summarized in the following table.

Mass absorption coefficients

	0.496A	0.561A	0.631A	0.710A	1.389A	1.539A	2.288A
Ne	.84	1.20	1.69	2.50	16.0	23.4	75.5
Al	1.96	2.71	3.82	5.32	37.3	50.7	149.6
SO_2	1.92	2.67	3.60	5.55	38.5	51.8	162.6
S(Calc)	3.40	4.64	6.89	9.96	66.4	88.4	284.0
Cl	4.14	5.76	8.18	11.52	76.9	102.7	315.0
A	5.06	6.89	9.80	13.0	85.7	114.0	339.4

25. The absorption of the $K\alpha$ line of carbon in various gases. ELMER DERSHEM AND MARCEL SCHEIN, *University of Chicago.*—The mass absorption coefficients of a number of gases for the $K\alpha$ line of carbon ($\lambda = 44.6$A) have been measured with the aid of a specially designed x-ray vacuum spectrograph in which a ruled grating was used to isolate the $K\alpha$ line. A photographic method was used and the densities of the photographic images obtained with and without gas in the chamber were compared by means of a photoelectric photometer. Pre-

liminary values of the mass absorption coefficients (μ/ρ) of the gases used are as follows He 3050; CO_2 4750; N_2 3950; O_2 5800; Ne 11500; SO_2 13000. Work on these and other gases is being continued and the above values may be slightly revised but are believed to be quite accurate.

26. The absorption coefficient of γ-rays from radium C and the effect of the rays on films. CHARLES S. BARRETT AND ROY A. GEZELIUS, *Naval Research Laboratory, Washington, D.C.*—The curve of film density vs. exposure is of the same type for γ-rays as for x-rays. The use of commercial screens of calcium tungstate reduce the exposures required in radiography with γ-rays to about 0.6 those required without screens; lead foil effects a reduction to about 0.75. The rapid increase in effectiveness of calcium tungstate screens with increasing hardness of rays in the x-ray region does not continue into the region of hard γ-rays. Recoil electrons from an aluminum sheet (optimum thickness about 2 mm) placed on the radium side of a film are not as effective for the above purpose as the electrons (chiefly photoelectrons) from lead foil. The linear absorption coefficient μ of γ-rays in iron was determined by densitometer measurements on films exposed under conditions similar to those of radiography, with precautions taken against scattered rays reaching the films from the rear. With blocks 30 cm square and 5–15 cm thick as absorbers and with films directly behind them, placed 45 cm from 250 millicuries of radon, $\mu=0.30$ cm^{-1}. This is in agreement with previous ionization measurements made under conditions where comparable amounts of scattered rays were present. A quantitative technique for γ-ray radiography has been worked out and is being published elsewhere.

27. A simple derivation of the formula for the half-width of the Debye-Scherrer lines. N. RASHEVSKY, *Westinghouse Research Laboratories, East Pittsburgh, Pa.*—In 1918 P. Scherrer published without proof the following expression for the half-width of the Debye-Scherrer lines:

$$h=2(ln2/\pi)^{1/2}\ (\lambda/l\cos\theta)=0.94(\lambda/l\cos\theta)$$

λ being the wave-length of the x-ray beam, l the size of the crystallites and θ the glancing angle. Seljakow and v. Laue independently gave later on rather elaborate analytical derivations of the above formula, their results differing from Scherrer's and from each others only in the value of the numerical factor (Seljakow—0.92; v. Laue—0.9). In the present paper a very simple and short derivation of the above formula is given, showing particularly clearly the physical cause of the broadening of the lines, and giving for the numerical factor the value 0.89.

28. The structure of some groups XO_3. W. H. ZACHARIASEN, *University of Chicago* (Introduced by H. G. Gale).—Through determinations of the crystal lattices of $KBrO_3$, $KClO_3$, $NaClO_3$ and Na_2SO_3 the size and the shape of the groups $(BrO_3)^{-1}$, $(ClO_3)^{-1}$ and $(SO_3)^{-2}$ were examined. These 3 groups show the same type of structure. This special type is also found for the groups $(AsO_3)^{-3}$ and $(SbO_3)^{-3}$ in the crystal lattices of As_2O_3 and Sb_2O_3 as determined by *Bozorth*. The structure type of the above 5 groups is distinctly different from the one of the groups $(BO_3)^{-3}$, $(CO_3)^{-2}$ and $(NO_3)^{-1}$. The cation is displaced an amount Δ out of the plane of the three oxygens, and this displacement can be expressed by: $\Delta=a/12(6)^{1/2}$, where a is the oxygen to oxygen distance in the equilateral triangle. Due to the existing relation between Δ and a, we can describe our type of groups as tetrahedral groups with one tetrahedral corner removed. Common for all groups of this type is that the cation has got only 2 electrons in the outer shell. The asymmetry which characterizes the configuration around the cation may be explained as due to deformation in the outer shell of the cation, where the charge distribution is very diffuse.

29. The building of atoms as related to nuclear abundance and stability. W. D. HARKINS, *University of Chicago.*—Recent investigations emphasize the importance of the rule that the elements of even atomic number are much more abundant than those of odd number. This and other evidence indicate that the most stable nuclei are those whose charge is represented by an even number. An even more important rule is that the most stable nuclei are those which

contain an even number of negative electrons. If the atomic species are divided into four classes according to the evenness or oddness of the number of nuclear electrons and protons, the most stable species are found to belong to Class I, for which these numbers, and the atomic number also, are even. The nuclear spin of all of the species of this class which have been investigated have been found to be zero. The nuclei of complex atoms in general seem to exhibit such relations as to indicate that with the possible exception of the alpha particle, they are built in steps. The particles which seem most likely to take part in increasing the mass of a nucleus are: the alpha-particle, the proton, the electron, the half alpha-particle $(p_2e)^+$, and possibly the neutron, although the last of these may not exist since the ratio of negative to positive electrons in a neutron is unity, which is abnormally high for a complex nucleus. The increase of mass by the addition of an electron may be negative on account of the packing effect.

30. Time lag in the formation of the latent image. LESTER I. ZIMMERMAN, *St. Louis University*. (*Introduced by F. E. Poindexter*).—Series of constant energy exposures were made on Hammer Extra-Fast plates at high and low light intensities by means of flashes of light from a rotating mirror for a range of mirror speeds. The time of illumination of the emulsion grain in each flash varied from 10^{-5} to 5×10^{-8} seconds. It was found that there was a gradual diminution of image density with decreasing time of flash until a critical flash interval was reached, after which the density-flash curve fell rapidly. The breaking point of the graph for high intensities was at a time of flash of approximately 1×10^{-7} seconds while that for the low intensity was 3×10^{-7} seconds. Assuming that the breaking over of the density-flash graphs is real, and not due to some undetermined characteristic of the apparatus, the conclusion is indicated that the formation of the latent image is a resonance process.

31. A study of the latent image at low intensities. FRANKLIN E. POINDEXTER AND LOUIS E. JAMES, *St. Louis University*.—Hammer Extra-Fast plates were exposed to light of very low intensities—the times for normal exposures ranging from thirty to two hundred and forty minutes. Two sources of light were used on each plate. A series of exposures was made with each source separately, a series of each on top of the other and, finally, a series was made when both lights were shining on the plate. It was found that the densities for the simultaneous exposures were in all cases greater than those formed by putting the image due to one source on top of the other. The difference between these densities, however, decreases with increasing intensities of the light sources. The results show that the failure of the reciprocity law is very appreciable even for fast plates at low intensities.

32. The band spectra of scandium-, yttrium-, and lanthanum monoxides. WILLIAM F. MEGGERS AND JOHN A. WHEELER, *Bureau of Standards*.—New data on wave-lengths and relative intensities of band heads in these three molecular spectra have been obtained and have been classified in a number of band systems resulting from transitions between various vibration levels of initial and final electronic states. For ScO 137 band heads are observed; these belong to 5 systems, the 0, 0 transitions of which are at I, 4857.79 and 4858.09A; II, 6017.07A; III, 6036.17A; IV, 6064.31A; V, 6079.30A. The YO spectrum closely resembles that of ScO; 126 band heads were observed; these are assigned to 5 systems with 0, 0 transitions at I, 4817.38 and 4818.20A; II, 5939.08A; III, 5972.04A; IV, 6096.78A; V, 6132.06A. In the LaO spectrum, more than 300 band heads have been measured; they appear to belong to 9 different systems. Our analysis of the LaO bands agrees in the main with that given by Jevons (Proc. Phys. Soc. London **41,** 520 (1929)). All of the bands in these spectra are degraded to red except two groups of LaO which are degraded to violet.

33. Regularities in the second spectrum of xenon. C. J. HUMPHREYS, T. L. DEBRUIN AND W. F. MEGGERS, *Bureau of Standards*.—A new description of the spectrum of ionized xenon (Xe II) has been completed; it gives wave-length and intensity data for about 1600 lines between the limits 2230A and 8716A. The ground doublet $(^2P_{1\,1/2,1/2})$ in this spectrum has been identified among lines observed in the Schumann region by Abbink and Dorgelo (Zeits. f. Physik **47,** 221 (1928)); the levels are separated by 10540 wave-numbers. This spectral term has been connected with others which combine so as to give lines in the visible Xe II spectrum,

and the absolute values of the terms have been fixed by extrapolating series-forming terms to their limits. The ionization potential is found from these spectroscopic data to be 21.1 volts.

34. Hyperfine structure patterns. S. GOUDSMIT AND R. A. FISHER, *University of Michigan.*—Hyperfine structure separations obey the interval rule very accurately. This enables one to construct simple graphs which represent all possible line patterns for given quantum numbers. Such graphs are useful in the interpretation of hyperfine multiplets especially in cases where not all components are resolved. They were successfully applied to preliminary measurements of Bi II hyperfine structure, recently obtained by us. Application to the partly resolved hyperfine multiplets of Mn I (H. E. White and R. Ritschl, Phys. Rev. **35,** 1146 (1930)) gives results which differ considerably from those obtained by White.

35. The transfer of energy between molecules during collisions: quenching of mercury resonance radiation by admixed thallium vapor. O. S. DUFFENDACK, *John Simon Guggenheim Memorial Fellow, University of Michigan.*—The quenching of mercury resonance radiation λ2537 by admixed thallium vapor was measured. At 0.8 mm mercury vapor pressure and 750°C the radius of the excited mercury atom has an apparent value 30 times greater than the normal kinetic theory radius. Previous measurements on quenching by permanent gases give a maximum radius 3 times normal. The addition of helium to the Hg-Tl mixture at 750°C permits the measurement of the quenching at 0.001 mm mercury vapor pressure and gives a radius of the excited mercury atom little greater than normal. When N_2 is substituted for He, the radius is somewhat greater. The differences are attributed to differences in the concentration of excited mercury atoms in the $^3P_1$ and $^3P_0$ states. The presence of metastable $^3P_0$ atoms makes the value of the average life of the excited atom uncertain.

The experiments indicate the possibility of isolating the effects of the $^3P_1$ state, in which case a radius very little greater than normal is probable: a result in agreement with estimates made from the quantum-mechanical theory of Kallmann and London (Zeits. f. Phys. Chem. **B2,** 207 (1929)). This investigation was carried out under the direction of Professor J. Franck at Göttingen.

36. The energy of dissociation of mercury molecules. J. G. WINANS, *University of Wisconsin.*—The absorption spectrum and the electrodeless discharge spectrum of mercury vapor between wave-lengths 2200 and 1550 were photographed with a fluorite vacuum spectrograph. In the absorption spectrum, three apparently continuous bands were observed with maxima at 1849, 1807, and 1685. With increasing pressure the 1849 band broadened symmetrically until it over-lapped the 1807 band. With further pressure increase the 1849 band broadened toward longer wave-lengths but retained a sharp short wave limit coinciding with the short wave limit of the 1807 band. In the electrodeless discharge excited by a low voltage Tesla coil, the bands at 1849 and 1685 were emitted, but not the one at 1807. Assuming that this failure of 1807 indicated that molecules which absorb 1807 are dissociated, potential energy curves for Hg_2 can be constructed to explain this. These same curves explain also the peculiar limitation of the 1849 band at the 1807 band. From these curves the energy of dissociation of Hg_2 is found as 0.20 volts. It is necessary to ascribe the 1807 band to an electron transition from a molecular energy level to an atomic energy level. This constitutes a new type of photochemical dissociation. Similar explanations have been made for the band spectra of zinc and cadmium. (Phil. Mag. **7,** 555 (1929).)

37. A spectroscopic study of the decomposition of organic vapors by the electrodeless discharge. DAVID M. GANS AND WILLIAM D. HARKINS, *Department of Chemistry, University of Chicago.*—When subjected to the electrodeless discharge, the vapors of organic compounds at pressures of several tenths of a millimeter of mercury are rapidly decomposed into monatomic and diatomic, neutral and charged fragments, with emission of light. Thus, for benzene, acetylene, and naphthalene, the spectrum reveals the presence of H and C atoms, C^+ ions, and C_2 and CH molecules. With aniline, the spectrum shows, in addition, the violet cyanogen bands, the β bands of NH, and the second positive (N_2) and first negative (N_2^+) groups of nitrogen. The spectrum for phenol contains the water vapor bands, due to OH, and the third

positive group of carbon, due to CO, as well as the decomposition spectrum typical of benzene. These very reactive fragments unite with each other to form brown to black solids of high molecular weight. Sufficiently unsaturated hydrocarbons are completely transformed into insoluble solids as rapidly as vapor enters the flask. Saturated hydrocarbons, like *n*-heptane, form little solid, since hydrogen is liberated, which raises the pressure and tends to extinguish the discharge. Besides dark solids, substituted benzene derivatives generally also give gaseous products, as water for phenol, ammonia or lower amines for aniline, and hydrogen chloride for chlorobenzene. Further work is in progress.

38. A continuous fluorescence emission spectrum which accompanies a change of color and the Raman spectrum. WILLIAM D. HARKINS AND H. E. BOWERS, *University of Chicago.*—In the study of the Raman spectrum of certain liquids a continuous emission spectrum has been found to appear, together with the Raman line spectrum, in each case in which the liquid becomes colored by the action of the radiation from the mercury arc light. The continuous spectrum was always absent when no such change of color occurred. The continuous spectrum was given by eight organic bromine derivatives of the paraffin series and by a solution of ammonia in methyl alcohol. The continuous spectrum is found between 3900 and 5200A, and between 5500 and 5800A.

39. Further study of the absorption of infrared radiation by water vapor. E. K. PLYLER AND W. W. SLEATOR, *University of Michigan.*—By making use of Echelette gratings, a Moll thermal relay and the spectrometer constructed by Meyer and previously described, the authors have re-examined with increased resolution the absorption bands of water vapor whose centers lie near 1.38μ, 1.87μ, 2.66μ, 3.17μ and 6.26μ. The new study has greatly increased the number of measured lines. Especially, near 6.26μ and 3.17μ the number has been more than doubled. The new lines are mostly weak ones, but the work has resulted in better determinations of the wave-lengths of many strong lines which now appear as sharp single effects freed from the former confusion due to overlapping. The center of the harmonic of the great band near 6.26μ is seen to be better placed at 3.168μ than as it was formerly at 3.11μ. It also appears that the band has no absorption at the center, and is of the doublet type like the fundamental.

40. Progressive relationships in the near infrared absorption spectra of the halogen derivatives of benzene. F. S. BRACKETT AND URNER LIDDEL, *Smithsonian Institution and Bureau of Chemistry and Soils, Washington, D.C.*—Automatic records of the near infrared absorption spectra of benzene and its halogen derivatives at an average resolution of 12A to the slit-width are offered. These spectra have been analyzed with respect to the second overtone of that fundamental vibration of benzene occurring in the region of 3.25μ, which probably approximates a linear oscillation of hydrogen with respect to carbon. In the progression benzene 8772 cm^{-1}, iodo-benzene 8780 cm^{-1}, brom-benzene 8787 cm^{-1}, and chlor-benzene 8800 cm^{-1}, a progressive shift to shorter wave-lengths of this second overtone occurring in benzene at the frequency 8772 cm^{-1} is observed. An explanation is offered based on the further reduction of electron density about the carbon centers resulting from the substitution for a single hydrogen of an increasingly electro-negative halogen in each case. Further shifts to shorter wave-lengths were predicted for the higher halogen derivatives. Spectra are offered of the three di-chlor, 1, 2, 4, and 1, 3, 5 tri-chlor, penta-chlor, and para- dibrom-benzenes, which in a general way substantiate these predictions. The general idea of relative decrease in saturation as correlated with increase of frequency is borne out. In the case of benzene, satellites are observed at frequencies occuring at multiples of 162 cm^{-1}. The presence of such a low frequency mode is consistent with the fine structure observed in the visible bands of benzene vapor.

41. Absorption bands of hydrogen halides in the liquid state. E. O. SALANT AND W. WEST, *Washington Square College, New York University.*—The (0, 2) bands of HCl, HBr and HI liquids and the (0, 3) of liquid HI, measured with quartz prism spectrometer, thermopile and galvanometer, show no rotational structure, centers of HCl and HBr bands being displaced to longer waves as compared with corresponding gas bands. The frequencies, with gas-liquid

displacements given in parentheses are, in cm^{-1}: HCl 5543 (125), HBr 4850 (180), HI 4262 and 6262. HI absorption, particularly, is strongly itensified in the liquid. With these values and the Raman lines (Salant and Sandow, Phys. Rev. **32,** 214 (1930)), the vibration frequencies and anharmonic coefficients of the vibrational terms are calculated for the liquefied hydrogen halides (the constants for the gaseous molecules, in parentheses, are from Birge, International Critical Tables, Vol. V):—ω_e: HCl 2800 (2991), HBr 2587 (2647), HI 2262; $x_e\omega_e$: HCl 8.5 (54), HBr 54 (44), HI 44. Differences between spectra of vapors and liquids are discussed. The frequency shifts of the hydrogen halides must be attributed not to a Lorentz-Lorenz force, but to some other, quantum mechanical interactions of the molecules (Breit and Salant, Phys. Rev. **36,** 871 (1930)).

42. Some effects of intense audio-frequency sound. NEWTON GAINES, *University of Texas* —Audible sound of great intensity is produced by magnetostrictive vibration of a nickel tube, two 250-watt radiotron tubes being employed in the apparatus. This sound is used to produce phenomena hitherto obtainable only with piezoelectric crystals vibrating at thirty or forty times the frequency and also entirely new phenomena. The nickel tube itself is vibrated so strongly as to rupture eventually at the middle. A five centimeter mound forms on the surface when the rod oscillates beneath water; this mound is *not* the result of radiation pressure. An air bubble released under water in the neighborhood of the vibrating rod becomes white, and under certain conditions moves against a strong stream of water. Carbon deposited on the sides of the nickel tube goes into colloidal solution when the tube is vibrated under water. The reaction of sonic radiation upon the radiator is demonstrated. Striations in a Kundt tube that are parallel to its axis are produced. Larvae are killed immediately by the sound; colon bacteria are killed, dying off in accordance with a simple logarithmic law. The irradiation of seed by the intense sound changes the rate of growth of the seedlings produced, usually retarding the growth but in certain cases accelerating it as much as 25 percent.

43. Supersonic interferometers. ELIAS KLEIN AND W. D. HERSHBERGER, *Naval Research Laboratory, Bellevue, D.C.*—The methods of applying high frequency sounds to small scale measurements are discussed. An interferometer was constructed and used to measure the velocity of sound in gases, liquids, and solids at frequencies ranging from about 10 to 700 kc. Three types of sources were tried, viz: quartz and rochelle salt crystals and magnetostrictive rods. The determination of the velocity of sound in solids are based upon (1) optimum transmission of sound through a partition whose thickness is an integral number of half wavelengths; (2) relative displacement of the nodal planes in a given liquid due to the immersion of the solid slab in the acoustical path. In the same manner, a small quantity of an unknown liquid is placed in a parallel walled cell and the latter is immersed in a liquid of known acoustic properties. Or, the variation in the velocity of sound with concentration of solution may thus be determined. Reactance and effective resistance of the interferometer (with a liquid medium) as a function of the reflector distance from the sound source were investigated. Approximate values of the impedance, power factor and watts dissipated in the instrument were thus computed. The use of the interferometer as a device for measuring supersonic frequencies is explained.

44. Sound absorption determined by transmission measurements. F. R. WATSON, *University of Illinois.*—A. H. Davis, (Phil. Mag. **50,** 75 (1925); **2,** 543 (1926)) has developed a formula for transmission of sound,—$I'/I=kW/as$, where I is the intensity of the sound incident on a partition, I' is the transmitted intensity, k is the coefficient of transmission, W, the area of the partition and as, the absorption of the surfaces in the receiving room. By suitable measurement of the ratio I'/I, it is thus possible to determine the absorption as. Preliminary tests by means of electrical instruments for the generation and reception of sound have given promising results, thus giving an instrumental substitute for the determination of the time of reverberation by the ear, as required by Sabine's method.

45. The rotating fluid in the relativity theory. EDWARD L. AKELEY, *Purdue University.* —The Einstein equations associated with the quadratic form

$$Adx_0^2+2Cdx_0dx_1+Bdx_1^2+J(du^2+dv^2)$$

where A, B, C and J are functions of u and v only, have been treated by a method which is a generalization of Weyl's theory of the axially symmetric field. The following transformation was used

$$A = e^{l+s}\cos\psi \qquad C = e^{l}\sin\psi$$
$$B = -e^{l-s}\cos\psi \qquad J = -e^{2}.$$

The theory of the rotating fluid was developed in this way. A power series expansion of the type $d = d_0 + d_1\rho + d_2\rho^2$ was used, where $d_2 = d_{20} + (\omega^2/\rho)d_{12}$; $d_3 = d_{30} + d_{22}(\omega^2/\rho) + d_{14}(\omega^4/\rho^2)$. ρ and ω represent respectively the density and the angular velocity of the fluid, and d_{ij} represents the coefficient of $\rho^i\omega^j$ in a double power series expansion in ω and ρ. The first approximation corresponds to the Newtonian theory. It is shown that there is a one to one correspondence between the figures of equilibrium in the two theories, and that the first approximation of the Einstein solution can be obtained from the Newtonian one. The second approximation predicts effects not included in the Newtonian theory. The field corresponding to that of the MacLaurin ellipsoid is developed to a second approximation. The relation of this treatment to the work of others is discussed.

46. Some physical properties of nitrogen. W. EDWARDS DEMING AND LOLA E. SHUPE, *Bureau of Chemistry and Soils, U. S. Department of Agriculture, Washington, D.C.*—The compressibility data on nitrogen obtained by Bartlett and coworkers are extrapolated to cover the range −70 to 600° up to 1200 atmospheres. A sensitive graphical scheme has been devised for obtaining $(dv/dp)_T$, $(dv/dT)_p$, $(d^2v/dT^2)_p$ at any point. It depends on the fact that the derivatives of $\alpha \equiv RT/p - v$ or $\Delta \equiv v(pv/RT - 1)$ enter as correction terms to the derivatives of v, just as α and Δ enter as corrections to v itself. Specific volume, density, coefficients of expansion $(-p/v)(dv/dp)_T$ and $(1/v)(dv/dT)_p$, fugacity, C_p, C_v, $C_p - C_v$, μ are calculated for the various temperatures and pressures. The calculations of C_p agree within 0.2 cal./mole deg. with the experiments of Mackey and Krase (J. Ind. and Eng. Chem. October, 1930) who worked to 700 and 800 atm. from 30 to 150°. The agreement is probably within the experimental error, but the trends of the two sets suggest that a real difference may exist. C_v decreases below 0°C at pressures up to 100 atm.; at higher pressures it increases. Experiment shows that along an isotherm $C_p = C_p^* + bp^2 + cp_3 + \cdots$, the first power of p being absent. It is found that C_p increases fairly uniformly from 10 to 100 atm. along isotherms between 20° and 200°.

47. The specific heat of methane. P. C. LUDOLPH, *University of Illinois.* (*Introduced by Jakob Kunz.*)—The specific heat of methane has been calculated for the tetrahedral model advanced by Dennison and for the symmetrical pyramid as worked out by Guillemin. The curve for the values obtained from the tetrahedral model has the same shape (linear) as the experimental curve but falls below it (as much as 5 cal./mole at 873°K). The values for the pyramidal model are still lower (9 cal./mole at 873°K). Another curve was obtained for the tetrahedron by redistributing the dimensions of the oscillators so as to get the largest possible values for the specific heat with the given frequencies. This curve is again linear but it still falls below the experimental curve. Some of the discrepancy may be due to an error in the experimental values which would tend to make this curve too high. It may be stated that the specific heat calculations of methane favor the tetrahedral structure.

48. Joule-Thomson effect in helium. J. R. ROEBUCK AND H. OSTERBERG, *University of Wisconsin.*—After completing the work with air (Proc. Am. Acad. **64,** 287 (1930)), the apparatus required extensive modification for use with helium. The effect of small proportions of air as an impurity was measured first, and as this proved very interesting the measurements were extended to the whole range of mixtures, all at the bath temperature 51.68°C, and inlet pressure 201 atm. The isenthalpic curve for pure helium is a straight line of negative slope, rising about 12°C per 200 atm. drop. As small quantities of air are added the curves do not change observably till possibly 10 percent air. With further increase in air the curves shift more and more rapidly over to about 28°C drop for pure air. Simultaneously the straight line for pure helium shifts over to the line, strongly concave toward the pressure axis, for pure air. The surprising result is the very small effect of the first addition of air and the increasing effect

of the equal later additions. Its pleasant aspect is that it effectually removes any worry as to the corruption of the helium data by air impurity. The isenthalpic curves for pure helium have been taken between the temperatures −100°C and +100°C. They are all straight lines of negative slope, and over this range the small erratic variation in the values of the slope exceeds any systematic variation. This value of μ is −0.060°C per atm.

49. A convenient laboratory source of hydrogen. G. W. SARGENT AND WHEELER P. DAVEY, *School of Chemistry and Physics, The Pennsylvania State College.*—Certain lines of research require considerable quantities of a reducing gas at rather infrequent intervals. In such cases the use of tanked or electrolytic hydrogen becomes unduly expensive. We are using a 1 to 3 mixture of nitrogen and hydrogen obtained by cracking NH_3. By slightly raising the outlet end of a 150 pound tank of liquid NH_3, gaseous NH_3 can be boiled off at room temperature, metered through an ordinary dry gas meter and cracked. We find it best to crack the gas in a nickel tube about 1/4 inch in diameter and about 12 feet long, coiled to fit inside an alundum tube which is heated to 1000°C by a nichrome winding. Slight traces of uncracked NH_3 are removed by passing the gas over about six feet of P_2O_5. The gas meter helps determine how much liquid NH_3 is left in the tank. A mercury relief valve by-passes any excess NH_3 into running tap water. A similar valve by-passes any excess H_2 into a pipe leading outdoors. These relief valves prevent dangerous pressures in the hot nickel coil. The apparatus is cheap and compact and gives a large storage capacity of H_2 in the form of liquid NH_3.

50. The deposition of dust on walls. W. J. HOOPER, *Battle Creek College.*—An apparent uncertainty exists in literature dealing with the cause for the peculiar deposition of dust on plaster and lath walls wherein the course of the laths and rafters behind the plaster is outlined in dust, popularly called "lath marks." Conclusive experimental proof of a thermal cause is given which is in agreement with the general theory of the behavior of small particles suspended in an atmosphere in which a temperature gradient exists.

51. Particle size of the disperse phase of nitrocotton solutions. WHEELER P. DAVEY, H. B. DE VORE, *The Pennsylvania State College and E. I. duPont de Nemours and Co.*—It is the purpose of this paper to report measurements made in 1927 on the particle size of nitrocotton in lacquer solutions, using the water-spreading method. (Davey, Science 1926, Eighth Colloid Symposium, 1930). Solutions of a given batch of nitrocotton in a mixture of ethyl acetate and ethyl alcohol would not spread satisfactorily on water at concentrations greater than 0.001 gm per cc. Measurements were taken down to concentrations of 7.8×10^{-6} gm per cc. The corresponding particle diameters were 3.69×10^{-7} cm and 1.54×10^{-7} cm. Over a considerable range the graph of particle diameter against logarithm of concentration is a straight line. Particle diameters at the lowest dilution are equal to about 20 atomic diameters of carbon, i.e. a maximum of about 140 nitrated glucose groups on the assumption of 2/3 complete nitration.

52. On the determination of principal stresses from crossed Nicol observations. R. V. BAUD, *Westinghouse Research Laboratories, East Pittsburgh, Pa.* (*Introduced by N. Rashevsky*).—The information obtained from crossed Nicol observations, combined with the differential equations expressing equilibrium requirements, is sufficient to obtain on basis of a graphical integration, the two principal stresses separately at all points of a "two-dimensional" model. When orthogonal curvilinear coordinates are employed, the differential equations contain the curvatures of the principal stress direction lines. Filon's method consists of expressing the curvatures by certain angles ψ, which he takes from the map of isoclinic lines. The author proposes that an additional map with lines ψ = constant be drawn, which procedure has certain advantages. When the paths of integration have one or more inflections, Filon's method is not entirely satisfactory. As an alternative, it is suggested to express the curvatures by the gradients $\partial\phi/\partial s$, or to measure the curvature by a curvature scale. A new method is suggested further, which consists in the use of polar coordinates. Crossed Nicol observations and "polar integration" combined appear to be the only existing method of studying stress distribution in rotating models. Even for static conditions preference will eventually be given to the "polar integration" in cases where the models have circular contours.

53. The effect of pressures up to 20,000 atmospheres upon some optical properties. THOS. C. POULTER, *Iowa Wesleyan College.*—This is a preliminary report and some of the data are of a qualitative nature. The rotatory power of a water solution of three sugars has been studied as effected by pressure. A rotatory power of ice VI has also been observed. The effect of pressure on the index of refraction of glass and of a paraffin oil has been studied.

54. On the change of the spectral composition of quasi-monochromatic radiation caused by scattering. OTTO HALPERN, *New York University.* (*Introduced by Richard T. Cox.*) It is shown that according to both the classical and quantum theories, there should appear in the scattered light from an ordinary quasi-monochromatic source frequencies corresponding to the proper frequencies of the scattering system and with an intensity of the same order of magnitude as that of the light scattered with unchanged frequency. The effect described affords a method of determining the spectral intensity of a line at an appreciable distance from its center of gravity. Reference is made to certain changes in hardness in the scattering of x-rays.

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Ellett, A. and R. M. Zabel—No. 1

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——— **and H. E. Bowers**—No. 38
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v. Laue, M.—No. 4
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Tyndall, E. P. T. and A. G. Hoyem—No. 12

Uhlenbeck, G. E. and L. A. Young—No. 3

Wahlin, H. B.—No. 11
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